

APPENDIX A

PROPOSED RESEARCH DIRECTIONS

Fossil Energy

**Reaction Pathways of Inorganic Solid Materials: Synthesis,
Reactivity, Stability**

**Advanced Subsurface Imaging and Alteration of
Fluid-Rock Interactions**

**Development of an Atomistic Understanding of High-
Temperature Hydrogen Conductors**

**Fundamental Combustion Science Towards Predictive
Modeling of Combustion Technologies**

REACTION PATHWAYS OF INORGANIC SOLID MATERIALS: SYNTHESIS, REACTIVITY, AND STABILITY

EXECUTIVE SUMMARY

Inorganic materials science today is critically lacking in the knowledge of predictive reaction pathway mechanisms that would allow the design and synthesis of materials with specified reactivity and properties. This is a complex and fundamental problem that affects all aspects of inorganic chemistry and materials science such as oxides, metals, alloys, catalysts, corrosion, degradation and thermal stability. Because the problem is so immense and affects such a wide range of materials, a truly integrated basic research approach of theory, modeling, synthesis, validation and testing is required. Success in merging these methods will allow for unprecedented control and predictability of properties and reactivity of technically relevant materials. It is proposed that the Office of Basic Energy Sciences (BES) invest in research programs that seek to determine the fundamental parameters necessary for predicting the reaction pathways of inorganic solid materials. The combined capabilities of the Department of Energy (DOE) national laboratories and the Nation's research universities will allow for the determination of a new set of principles by which inorganic solids research can be governed. The reliable prediction of the reactivity and properties of materials will foster a new fundamental science, while significantly contributing to applications that improve U.S. energy security.

Current understanding of chemical bonding provides a set of "governing rules" that correctly predict the reaction mechanisms and products for organic chemistry. Such is not the case for solid inorganic chemistry/material science due in part to the complexity of the systems being studied (i.e., compositional variability, defects, electromagnetic interactions, metastability, and cooperative interactions). Illustrative examples of the sensitivity of materials performance to compositional/defect variability include: (1) a chromia-forming heat-resisting alloy with a variation of only 0.5 wt% Si doubling its life span for protective-scale formation under thermal-cycling conditions, and (2) small variation of elemental composition and defect structure of ionic conducting perovskites increasing performance.

Recent advances in materials modeling, synthesis and analytical capabilities provide a strong foundation for significantly advancing understanding of reaction pathways of inorganic solid materials. For example, density functional theory (DFT) allows us to study complex heterogeneous systems and reveal energetically favorable structures, embedding techniques and hybrid methods that capture dynamics allow study of extended systems, and cluster variation method (CVM) calculations allow for predicting the phase equilibria in multicomponent alloys. Synthesis methods have progressed substantially beyond "ball-milling and heating" to procedures that take advantage of new breakthroughs in nanoscience, such as low-temperature synthesis of metastable phases, self-assembly and epitaxial growth of thin films that access previously unachievable phases. Analytical capabilities such as calorimetry of transition metal oxides and neutron science (inelastic neutron scattering of metastable phases and reactions in-situ) allow for fundamental probes of phase formation and kinetic interactions in reactions. Microspectroscopic methods such as X-ray emission and scanning probe microscopies, together with more recent techniques such as 3-dimensional atom probe, will allow study of individual sites with unprecedented energy and temporal resolution.

The knowledge gained through this coordinated technical approach will have significant impacts on fossil energy science and beyond. Understanding the rules that control the synthesis, reactivity and stability of inorganic materials will allow substantial improvements in a wide variety of fossil energy applications in-

cluding sensors, reliable and durable structural materials for high-temperature applications, membranes, and catalysts. Additional impacts will include energy sources (hydrogen) of the future, legacy clean-up and long-term waste storage and actinide science relevant to the DOE-Defense Program's (DP's) mission.

Summary of Research Direction

Inorganic materials science today is critically lacking in the knowledge of predictive reaction pathway mechanisms that would allow us to design and synthesize materials with specified reactivity and properties. Currently, an "Edisonian" approach is the most common method for directing materials synthesis toward an intended bulk property, with structure/property relationships usually being determined in the post-analysis. This is a non-optimized approach without much predictive capability. Furthermore, this is a complex and fundamental problem that affects all aspects of inorganic chemistry and materials science such as oxides, metals, alloys, catalysts, corrosion, degradation and thermal stability. An integrated basic research effort by academics and national laboratory scientists will combine theory and experiment, using state-of-the-art DOE user facilities to address the following questions:

- What chemical forces drive the operative reactions (e.g., crystallization of unique phases) and can, with the understanding these forces, lead to the synthesis of other classes of materials?
- What chemical mechanisms are responsible for observed bulk properties (e.g., ionic conduction, multicomponent diffusion, or catalytic selectivity)? What are the atomic-scale origins of reactivity in these materials?
- How will understanding atomic-scale properties/phenomena, such as atom-atom and atom-defect binding energies, nearest-neighbor interactions, site selectivity and changes in crystal structure, lead to the synthesis of new classes of tailored inorganic phases?
- How will understanding 1-dimensional and 2-dimensional structural defects in materials lead to the synthesis of materials with tailored properties?
- How can the thermodynamics of systems with stress-mediated interactions and consequential non-equilibrium effects at the interface be properly treated?
- Can interface mobility, as a function of its structure, orientation, composition, and strain field, be accurately modeled? Included here is the growth of a faceted interface (dynamics of step propagation).
- What nontraditional transformation pathway processes need to be established to describe the selection of stable or metastable phase(s) and the advancement of corresponding laws of phase transformations?

The goal of this type of program is detailed understanding of the atomic mechanisms (or reaction pathways) responsible for the formation of inorganic phases and the ability to predict the bulk properties of those formed materials. This general approach is a necessary goal for all areas of inorganic chemical research, including solid inorganic oxide, and metal and alloy chemistry/material science. Examples of areas of need include:

- In the area of ionic conducting perovskites, variation of elemental composition and defect structure increases performance. Existing methods for synthesizing perovskites, and those with high dielectric constants and/or ionic conductivity include ball milling and heating, ball milling to release an exotherm plus heating, solgel synthesis and thin film applications, solgel plus organic addition synthesis (for high surface area materials), and metalorganic chemical vapor deposition. All these methods involve high-temperature heating, necessary for perovskite crystallization. This is not only costly in heating costs, but also adversely affects the final material. Research into low-temperature perovskites derived from stoichiometrically predetermined metastable phases (i.e., solgels, molecular sieves) are different energetically, and probably show more ionic disorder (i.e., metastable which is desirable for properties such as ionic conductivity and high dielectric constant) compared to materials synthesized directly at high temperature. This gives the ability to “tune” the resultant perovskite into novel compositions.
- In the area of synthesizing materials with tailored properties, it is well established that properties are inextricably linked to the micro- and/or nano-structure of a given material. The evolution of a micro- and/or nano-structure often involves self-organized phenomena, which can result in highly regular structures of controllable geometry and size. Although there are multiple routes to self-organization, involving different driving forces, length scales and system dimensionality (i.e., whether 2-d or 3-d), it is important to understand the underlying principles, which universally describe self-organization, irrespective of the specific details of the system.
- In the area of heat-resisting alloys, slight variations in alloy composition can significantly affect resistance to high-temperature degradation and, hence, performance. This is true even for composition variations within the specifications of a commercial alloy. Such a sensitivity to composition reflects the complex interactions of alloying elements on scaling behavior, scale adherence and cracking/spallation behavior, and subsurface diffusion behavior. A holistic approach that addresses all these aspects of high-temperature degradation needs to be taken if there are to be any leap-frog advances in improving the reliability, durability and predictability of alloys and coatings for high-temperature applications.

New Scientific Opportunities

New scientific opportunities exist in the combination of basic synthetic research methods, plus analytical abilities to understand from the reaction pathway level of interactions of reactants to their effect on bulk properties. This is the opportunity for modeling experts to use expanded modeling/simulation codes on ever more powerful computers to predict the true events in these complex materials systems (e.g., see Figure 1-1), and to utilize embedding techniques and hybrid methods that capture dynamics for the study of extended systems.

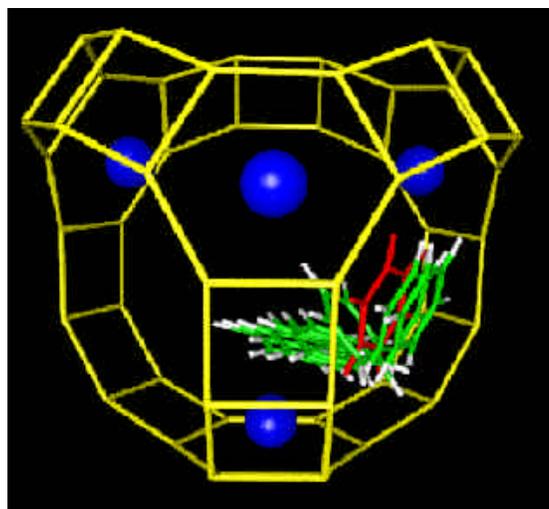


Figure 1-1. Minimum Energy Path for Benzene in NaY Zeolite (between a cation site and the window site). [Auerbach, *Int. Rev. Phys. Chem.* 2000, 19, 155].

Recent progress in synthetic methods allows for the exploration of new phase space areas, particularly in low-temperature synthesis of metastable phases by hydrothermal and *chemie douce* methods, self-assembly of inorganic oxides and III/V semiconductors through organic molecule capping techniques, and epitaxially growth of thin films. Studies of the synthesis, its optimization and the mechanism of formation will need the combined efforts of X-ray (i.e., synchrotron) and neutron scattering technologies. An excellent example is the use of time-resolved studies at the National Synchrotron Light Source (NSLS) and Advanced Photon Source (APS). Time-resolved studies would allow us to study structure transformation between metastable phases through to thermodynamically stable phases. Fundamental issues to be studied include structure, mechanisms for transformation (i.e., bond breaking), and microporosity durability versus structure densification, through the observation of the reaction from gelation to crystallization using time-resolved scattering. The ability to observe metastable intermediates directly, some of them existing for just a short time, is a distinct advantage and an excellent complement to the exploratory synthesis efforts.

Relevance and Potential Impact

This proposed research direction is of direct relevance to all energy programs (e.g., Fossil, Nuclear, Energy Efficiency, Renewable, Fusion).

The knowledge gained through this coordinated technical effort will have significant impacts on fossil energy science and beyond. Understanding the rules that control the synthesis, reactivity and stability of inorganic materials will allow substantial improvements in a wide variety of fossil energy applications, including sensors for monitoring in high-temperature and caustic environments, reliable and durable structural materials for high-temperature applications in advanced power generation systems, materials and coatings for supercritical reactors, membranes for ionic/proton conduction and hydrocarbon feedstock separations (allowing for the removal of costly distillation units), and catalysts for vastly increased energy and economic efficiency plus reduced environmental impact.

Additional impacts will include energy sources (hydrogen) of the future, legacy clean-up and long-term waste storage and actinide science relevant to the DOE-DP mission. In particular, the fields of proton and ionic conductors have been hampered by “Edisonian” approaches for synthesizing better conducting materials. Instead of traditional human combinatorial approaches, the employment of defined reaction pathways will be used in the design and tuning of high-conducting oxides with built-in thermal, mechanical and chemical stability. Furthermore, the resultant reaction pathway rules will be employed in the synthesis of materials for waste legacy clean-up and long-term waste storage of radioactive solvated nuclei found today in temporary waste storage facilities around the country. Finally, the application of this predictive knowledge to actinide science allows for safe, non-repetitive synthetic laboratory procedures, resulting in minimized exposure to workers.

Estimated Time Scale

The determination of the fundamental parameters of the reaction pathways for inorganic solid materials resulting in predictive synthesis, reactivity and stability is a long-term goal of the basic research community. Achieving this goal has yet to be accomplished due to the significant complexity of the problem. The full cooperation of basic research scientists from national laboratories and academic communities, plus full use of the DOE’s user facilities, will be needed to make any notable headway. We believe that with full cooperation and funding in 3-5 year increments, this will be a 10-20 year investment for BES.

ADVANCED SUBSURFACE IMAGING AND ALTERATION OF FLUID-ROCK INTERACTIONS

EXECUTIVE SUMMARY

Fossil energy resources are currently the backbone of the U.S. energy system, and their continued availability in the short term is critical for maintaining U.S. economic security. The technically recoverable reserves of oil and natural gas are many times those of current proved reserves. Advanced geoscience technologies will enable industry to meet the challenges of locating and extracting these additional reserves in an environmentally acceptable and cost-effective manner. Two research areas that would have major impacts are subsurface imaging and in-situ alteration of fluid/rock interactions. Subsurface imaging will delineate deep geologic structure and the properties, composition, and spatial distribution of rocks and fluids. Research supporting imaging would have application to hazard prediction, resource quantification and reservoir process monitoring. Purposeful in-situ alteration of rock/fluid interaction deals with technologies for increasing the mobility of oil and gas phases, thereby increasing the amount of extracted resources. It also deals with development of technologies which will ultimately enable in-situ processing of hydrocarbons, replacing processing steps that are currently carried out on the surface.

These advanced geoscience technologies will require development of new fundamental understanding of geophysical, geohydrologic, and geochemical processes. Fundamental research in wave propagation and new mathematical methods for inversion of geophysical, geohydrologic, and geochemical data will provide part of the basis for major advances in imaging. Other basic research is needed to understand how to predict processes from measurements at different scales. Exotic physical phenomena such as electrokinetic and seismoelectric effects need to be assessed through basic research to identify technological applications. The basic processes controlling the mobility of one fluid phase relative to another need to be understood. Finally, the possibility of using nanoparticles to alter rock/fluid interactions, thereby either increasing mobility of oil or releasing more easily extractable volatile gas, opens the door for revolutionary new hydrocarbon extraction technology.

Successful application of this basic research will have major scientific payoffs within the next two decades as well as potential financial impacts in the energy industry of billions of dollars per year.

Summary of Research Direction

Advanced geoscience technologies are necessary in order to meet the challenges of environmentally acceptable and cost-effective extraction of remaining domestic reserves of oil and gas and to enable development of unconventional reserves. Two areas that would have a major impact on reserve extraction are subsurface imaging and in-situ alteration of fluid/rock interactions. Major advances in these technologies will require development of new fundamental understanding of geophysical, geohydrologic, and geochemical processes.

Subsurface imaging will delineate subsurface geologic structure and the properties, composition, and spatial distribution of rocks and fluids. By repeating measurements over time, hydrodynamic, geochemical, and geomechanical processes can be monitored. Research supporting imaging technologies would have application in at least three major areas: (1) hazards prediction, (2) resource quantification, and (3) monitoring of reservoir processes.

Improved imaging will reduce the risk of siting and drilling wells. Hazards include overpressure; weak unstable materials, such as shallow water flows; and salt, which creeps. Imaging research needs to focus on providing quantitative information on the physical properties of hazards as well as location and spatial extent.

Subsurface geophysical imaging has been used for decades to identify the location and quantity of oil and gas resources. In conventional oil and gas fields the challenge is now to locate smaller pools which have been missed during original exploration. Unconventional gas resources such as coal bed methane and methane hydrates present new challenges. In neither case are conventional oil and gas imaging technologies adequate to quantitatively evaluate the amount and distribution of the resource.

Monitoring of reservoir processes will enable more cost-effective production as well as provide information on additional reserves. Information is needed on the changes over time in the distribution and pressure of oil, gas, and water during primary, secondary, and tertiary production. Injection of chemically reactive substances, such as CO₂, necessitates geochemical monitoring as well. Imaging for monitoring requires the combination of direct measurement of quantities, such as chemical composition, pressure and fluid flux with indirect geophysical measurements. Research is needed to develop methods that integrate the various types of data in developing an image, as well as to improve resolution and quantitative interpretation of imaging results.

Purposeful in-situ alteration of rock/fluid interactions is the second research area that could have major impacts on oil and gas recovery. Primary production of oil and gas is carried out utilizing natural forces such as differential fluid pressure, gravity, and reservoir compaction. Injection of water, steam, CO₂, or other chemicals are used for secondary and tertiary recovery of oil, and are examples of purposeful alteration of rock/fluid interactions.

Most secondary and tertiary methods involve modification of the mobility of one phase relative to another. Wettability describes the relationship among mineral surfaces and the immiscible fluid phases. It strongly influences the location and distribution of fluids and fluid relative permeabilities and is one of the main design parameters for selecting the best recovery strategy. Nonetheless, the complex mechanisms controlling wettability and its effect on oil recovery are not well understood.

It has been suggested that phase mobility can be modified by low-frequency seismic energy, diffusive pressure waves, and electrokinetic and seismoelectric phenomena. Research is needed to evaluate fundamental mechanical, hydrodynamic, and electrochemical processes that may change the mobility of one fluid phase relative to another.

The possibility of using nanoparticles to alter rock/fluid interactions, and, in particular, increase oil mobility, represents a new, potentially significant research direction. For example, oil might be sorbed onto nanoparticles which would have lower capillary forces than the unmodified oil. Another technique might be to use nanoparticles that would adhere to pore surfaces but present hydrophilic surfaces to the oil. Finally, tailoring electronic properties of nanoparticles opens the door for developing materials, and perhaps slight variants of natural minerals, that would have unique catalytic properties. It may then be possible to break long-chain hydrocarbons in place, releasing more easily extracted volatiles.

New Scientific Opportunities

Research directed toward subsurface imaging and alteration of fluid rock interactions will provide opportunities for broadening and developing new areas of fundamental science in geophysics, geohydrology, and geochemistry.

Fundamental research in wave propagation in complex media will provide understanding needed to make advances in imaging. The complexity of rock masses arises from the existence of discontinuities such as fractures and faults, which exist at all scales, heterogeneity in lithology arising from natural geologic processes such as deposition, intrusion, and hydrothermal alteration, and the presence of fluids of different phases and properties that are heterogeneously distributed at all scales. For such media, the relative contribution of scattering and intrinsic attenuation to frequency dependent changes in amplitude needs to be better understood. New rock physic models are needed that quantitatively describe intrinsic attenuation in porous rock containing heterogeneous distribution of fluids of multiple phases. New models for wave propagation at a macroscopic scale that accurately capture effects of different loss mechanism, need to be developed. Differences in the models for different geologic environments need to be understood. Factors affecting wave-propagation are expected to be very different in sand, shale, soil (unconsolidated sediments), coal, and granite.

Electrokinetic phenomena, and in particular, seismic-electric, and electro-seismic coupling are not well understood. Prediction of behavior at the macroscopic, or field scale, is particularly uncertain. Diffuse pressure waves, which travel primarily in the fluid phase, are also not well modeled and characterized. Further fundamental work on these phenomena could lead to new imaging methods. These same phenomena may also have effects on phase mobility which could lead to breakthrough technologies for enhanced recovery of oil and gas resources.

The non-uniqueness of inversion is a fundamental problem in imaging. Joint inversion of various types of data is one approach to the problem of non-uniqueness, but joint inversion is computationally intensive. New mathematical approaches, including support vectors and other new algebras, need to be explored.

Fundamental research needs to be focused in geophysics, geohydrology and geochemistry on issues of scale in complex media. It is not clear how to scale geophysical measurements from the laboratory scale to field scale. It is not clear how to combine hydrologic models of processes at the microscale in pores and fractures to generate effective media models applicable at field scale. It is not well understood why fluid/rock reaction rates determined at laboratory scale experiments are up to several orders of magnitude faster than similar reaction rates measured at field scale.

Advancements in purposeful alteration of rock/fluid interaction requires new fundamental understanding of the mechanisms controlling wettability in reservoirs. Scientific opportunities include: (1) understanding influence of asphaltenes and oil composition on wettability, (2) studies of effects of brine composition, (3) studies of clay and colloid particle content and composition, and (4) understanding influences of colloid-interface associations.

Finally, the potential for development of new approaches to alter fluid/rock interactions using nanoparticles provides a whole new area of nanoscience research opportunities. Very little is known about the properties of mineral nanoparticles that would be most applicable, although several expectations arise from what is known about semiconductor nanoparticles and crystals. The electronic properties of nanominerals are

size dependent and not the same as the bulk structure of the same material. Surface properties such as surface tension and hydrophobicity/hydrophilicity are also size dependent. Chemical modification of nanoparticle surfaces may be possible that would enable unique collective phenomena such as aggregation. All of these properties may be tailored for enhanced recovery applications.

Relevance and Potential Impact

Fossil energy resources are currently the backbone of the U.S. energy system and their continued availability in the short term is critical for maintaining U.S. economic security. It is well known that domestic oil reserves and oil production are declining. Conventional production of natural gas in the U.S. may peak as early as the year 2015, though natural gas consumption is increasing faster than any other fossil fuel. Though the current proved domestic reserves of crude oil and natural gas are 22 BBO (billion barrels oil) and 177 TCF (trillion cubic feet), the technically recoverable reserves are 175 BBO and 1431 TCF, respectively. In 1995, the United States Geological Survey (USGS) estimated that over 50% of the technically recoverable oil reserves is oil in known fields that could be added through field extension, additions of new pools and application of new recovery techniques. Even 90 BBO is a large increase in oil reserves. Major breakthroughs in imaging and new advances in purposeful alteration of rock/fluid interactions will provide the technology needed to cost effectively locate and extract much larger percentages of the technically recoverable resources. Financial impacts of technology breakthroughs in the energy industry are measurable in terms of billions of dollars per year.

Estimated Time Scale

It is extremely difficult to forecast technology breakthroughs. It is envisioned that research will be continuing in each of the areas discussed for decades. At the same time, useful results will be generated over the course of continuing research efforts. Whether by incremental advancement of knowledge or major breakthroughs, major payoffs would be anticipated during the next two decades.

DEVELOPMENT OF AN ATOMISTIC UNDERSTANDING OF HIGH-TEMPERATURE HYDROGEN CONDUCTORS

EXECUTIVE SUMMARY

Ion transport membranes composed of proton-conducting materials are a critical component for future fuel processing and energy production systems, as well as ancillary technologies such as fuel cells, sensors, and electrolyzers. Proton conducting membranes are necessary to extract *absolutely* pure hydrogen from mixed gas streams in the processing of fossil fuels and other petroleum and petrochemical processes. The best candidate membrane materials for hydrogen separation at high temperatures are proton-conducting ceramic oxides. However, despite great efforts, a viable ceramic-based proton conductor has not yet been developed. The objective of the proposed thrust is to develop, through the integration of theory, modeling, and experimentation, a scientific understanding of the mid- to high-temperature (<600°C and 700°C) interaction of incorporated hydrogen with the host atoms and structural defects in a new class of oxides and amorphous metallic proton conductors.

Current science and future facilities are well positioned to make these advances. For instance, the more advanced computing systems are providing powerful tools for research through massively parallel implementations of simulation models. High-performance computing is enabling researchers to model materials systems at reduced dimensionality, while at the same time accurate first-principle calculations of materials properties now extend to systems involving thousands of atoms. The advent of powerful pulsed neutron sources is making possible the acquisition of neutron diffraction data on much shorter time scales. These and current neutron facilities will provide the capability to shorten the time scale to tens of seconds for some materials systems as well, which will allow for critical time-resolved in-situ studies of protonic conductors. Specifically, neutron diffraction can be used to locate the coordinates of oxygen and hydrogen (deuterium) ions in bulk polycrystalline solids, which are essential to the conductivity of these materials. This will expand the scientific understanding required to optimize the structure-related properties of crystalline, nanocrystalline, and even amorphous materials for gas separation, hydrogen storage, fuel cell, and other economically important applications.

The advances made by this effort over the next 10 years are critical for the leap-frog development of novel ion conducting oxides and alloys for hydrogen separation membranes. Such a development will allow for the recovery of millions of cubic feet of hydrogen at refineries every day and thus save the petroleum, steel, and petrochemical industries hundreds of millions of dollars annually. It will also facilitate the separation of hydrogen from carbon-dioxide-laden streams, facilitating sequestration.

Summary of Research Direction

A more fundamental understanding is needed of how hydrogen is transported and stored within the atomic lattice, at interfaces in crystalline materials, and within the disordered structure of bulk amorphous metals. Neutron sources offer exciting new opportunities for studying the migration and storage mechanisms for hydrogen in various materials. The ability to also conduct *in-situ* analysis to examine the influence of temperature and environment on transport processes and stability issues will play a major role in developing the next generation of hydrogen conductors. Theoretical studies utilizing such information will be needed to provide a basis for tailoring materials and multicomponent systems. Opportunities also exist for

developing new materials by gaining further insights into the behavior of nanocrystalline oxides and bulk amorphous alloys.

New Scientific Opportunities

Proton Conductors. Proton conductors are critical materials for future hydrogen-fueled systems and the related infrastructure required to produce and deliver hydrogen. These can be used as solid electrolytes in fuel cells, ionic membranes and gas sensors. However, the properties of current materials are not sufficient to meet the needs for commercial applications. To date, the available materials are not sufficiently stable in the anticipated service environments and lack the high protonic conductivity and enhanced catalytic properties required. Future research efforts must focus on the fundamental understanding of hydrogen conduction and storage mechanisms and their relation to composition and crystal structure to uncover new protonic conduction materials.

All current proton conductor systems have issues related to insufficient chemical stability and proton diffusivity and/or the dominance of other charge carriers to the total electrical conductivity. For example, hydrate compounds such as $\text{H}_3\text{Mo}_{12}\text{PO}_{40}\cdot\text{H}_2\text{O}$, $\text{HClO}_4\cdot\text{H}_2\text{O}$, which possess high protonic conductivity, are unstable in dry atmospheres and at temperatures above 100°C. A similar situation is found with the bronze-structured H_2WO_3 or H_xMoO_3 oxides. Despite the fact that these materials have high proton mobility, their electrical conductivity is dominated by the electronic contribution, and protonic conductivity is not major factor in this case. In acceptor-doped perovskites (e.g., SrCeO_3 , BaCeO_3), the electrical conductivity can be enhanced by trivalent dopants that introduce oxygen vacancies and promote the incorporation of protons. Unfortunately, the ratio of hydrogen-to-oxygen transport diminishes at elevated temperatures, and the materials are no longer effective hydrogen conductors.

A major issue is the need to discover materials that are capable of hydrogen storage levels of $\sim 10\%$. Studies of proton storage in oxides indicate that the protons are associated with the oxygen in the lattice and form OH groups in concentrations of only 3-5%, concentrations that are comparable to the oxygen vacancy content. Similarly, the hydroxides such as LiOH can store only $\sim 4\%$ hydrogen, while some of the hydrides are reported to store levels approaching 10% but have issues with stability.

Oxide Conductors. In the case of oxide proton conductors a new paradigm is required to overcome past deficiencies. Unique crystal chemical approaches are envisioned to enhance proton conductivity including (1) introduction of vacancies and defects through novel doping schemes; (2) nonlinear enhancement of properties in compositions near phase boundaries; and (3) exploitation of interfacial effects in multiphase compositions in combinations of chemically related but crystallographically dissimilar proton conductors, such as those with layered structures. Another area for research is the development of ion-conducting thin films, which could accelerate the application of proton conductors as ion separation membranes by enhancing hydrogen permeability, even at lower operation temperatures. There is potential for achieving such goals by developing thin film membranes with thickness less than one micron on porous substrates. This could lead to devices with much higher permeation rates than the current devices that utilize one to two millimeter thick bulk membranes.

While this is insufficient, there is an extensive experimental database on perovskite structures, which could serve as the initial basis for developing new oxide systems. The advent of new neutron beam lines will provide a powerful means for establishing the mechanisms of hydrogen storage and transport in these and

other oxide lattices. For instance, quasi-elastic neutron scattering could be employed to study the proton-phonon interactions and develop new insights into protonic transport at the atomistic level. This will also require the development of models and analytical tools to be able to interpret such data. Such advances will allow one to examine the real effects of specific dopants on proton transport and provide for critical in-situ studies of the effects of temperature and gas composition. These results would be linked with theoretical studies utilizing first principles and various longer length scale approaches (e.g., molecular dynamics) to describe the role of lattice structure and composition in vacancy formation and the storage and transport of hydrogen within the lattice. With such understanding, it will be possible to develop materials where electrical transport is not limited by lattice diffusion.

In addition, there is a need to search for and take advantage of new mechanisms for protonic transport. There is the potential for novel nanocrystalline oxides as hydrogen conductors. Studies have shown that nanocrystalline perovskites (e.g., Yb-doped SrCeO_3) can exhibit over a thousand-fold increase in electrical conductivity, as compared to the conventional micron-grain-sized ceramics. This effect may be related to the more rapid diffusivity expected to occur along grain boundaries in comparison to that through the lattice. In addition at a grain size of 10 nm, the grain boundaries constitute a substantial fraction of the material. This suggests that nanomaterials may have untapped potential for greater hydrogen storage together with more rapid transport.

A new class of hydrogen separation materials may be possible through the synthesis of bulk amorphous alloys and nanocrystalline metals. Metallic alloys in noncrystalline states generally contain significant “free volume” at the atomic scale that may facilitate hydrogen storage and transport in a controlled fashion. Studies in the past of these materials have been limited due to metastability of these alloys. However, stable forms have been demonstrated that enhance their potential for consideration as proton conductors. Thus, bulk amorphous alloys constitute a new and exciting class of metallic materials with unique physical and mechanical properties for functional and structural uses.

Relevance and Potential Impact

For the next several decades, H_2 will be generated from fossil fuels until clean H_2 sources can be developed. Pure H_2 streams will need to be produced via separation from mixed gas streams containing CO , CO_2 , H_2O , hydrocarbons and other gases by separation processes. There is a tremendous need for H_2 separation membranes if the H_2 infrastructure is to become a reality. Pure H_2 is needed for fuel cells, to facilitate H_2 storage, to recover H_2 from mixed gas products in the petrochemical industries, and for upgrading of petroleum products to fuels. In the next several decades more H_2 will be consumed converting petroleum into fuel than any other end use. However, at present there are no viable high-temperature separation membranes capable of producing pure H_2 streams. This area of research needs to be rapidly expanded over the next decade if the H_2 economy is to become a reality.

Estimated Time Scale

Improvements in current materials might be accomplished through such studies over the next five years. However, the evolution of new material classes for hydrogen conductors is likely to require another decade of fundamental research.

FUNDAMENTAL COMBUSTION SCIENCE TOWARDS PREDICTIVE MODELING OF COMBUSTION TECHNOLOGIES

EXECUTIVE SUMMARY

The development of predictive computational capabilities for combustion devices is a long-term goal of the DOE that has yet to be realized due to the magnitude of the scientific and computational challenges presented by turbulent, chemically reacting systems. Continuing advances in high-performance computing and laser diagnostics provide an unparalleled opportunity to advance combustion science, leading to science-based engineering design methods that will revolutionize the performance of combustion systems. An integrated program of basic theoretical, computational, and experimental research is needed bring the fundamental understanding of combustion science up to the level needed to provide a basis for predictive computational models for complex combustion systems. This program should involve closely coupled research by scientists at universities and national laboratories using terascale computers, state-of-the-art laser diagnostic capabilities, and web-based tools for data sharing and collaboration. Emphasis should be placed on the chemical kinetics associated with ignition, combustion, and pollution formation in realistic fuels and on the physics of the coupling of turbulent fluid dynamics with chemistry. An integrated approach is required to connect the various aspects of fundamental science needed to address complex combustion systems.

Combustion of fossil fuel is central to the U.S. economy, accounting for \$334 billion in fuel costs in 1996 and 85% of annual energy consumption. Combustion of fossil fuels is also responsible for nearly all of the anthropogenic emissions of nitrogen oxides (NO_x), carbon monoxide (CO), soot, aerosols, and other chemical species that are harmful or are suspected to be harmful to human health and the environment. At the global level, fossil fuels will continue to be the primary source of energy required for economic growth. Issues of energy security, global economic competitiveness, public health, and environmental integrity will have a profound impact on the design and operation of the combustion systems of the future. For example, radically new engine designs are the only hope for meeting the near-zero NO_x and particulate emissions commitments proposed for implementation by 2012.

The traditional evolutionary approach to combustion system development, which relies heavily on cut-and-try engineering to test incremental design changes, is inadequate to meet these challenges. A major barrier to rapid development of radically new combustion technologies with reduced emissions and improved efficiency is the absence of truly predictive computational tools for combustion systems. The phenomena that influence combustion span wide ranges of scales in both time and space. Consequently, no foreseeable computational hardware will be capable of running a fully resolved and coupled simulation of combustion in a practical combustion device, which includes detailed chemistry and all scales of turbulent fluid motion, with turnaround times fast enough for design calculations. Physically accurate and computationally efficient models are needed that are based on fundamental combustion science and validated rigorously against detailed experiments. However, there are significant gaps or uncertainties in our knowledge of the relevant chemical kinetics and in our fundamental understanding of the complex dynamic coupling of turbulent flow, molecular transport, and chemical reactions. Today's most advanced turbulent combustion models can only predict simple flames with reliable accuracy. Accurate prediction of phenomena such as soot formation, auto-ignition of turbulent mixtures, local flame extinction and re-ignition in complex flow geometries, flame

propagation in heterogeneous mixtures, and stabilization of detached flames will require greater scientific understanding and further development of combustion models.

Science-based predictive capability for complex combustion systems will revolutionize the development of future combustion technologies by moving much of the innovation, design, and optimization process onto the computer. It will facilitate the exploration and development of radically new concepts for high-efficiency, low-emission devices for conversion of fossil energy. It will also greatly reduce the time required for industry to bring new technologies to market or adapt designs to accommodate specific operational requirements, such as fuel flexibility.

Summary of Research Direction

The phenomena that influence combustion span a wide range of scales in space and time. The spatial scales extend from the dimensions of molecules, where chemical reactions occur, up to the scale of the combustion device itself. Temporal scales extend from those associated with the fastest chemical reactions to the residence time of fluid in the combustor. No foreseeable computational capability will be able to encompass phenomena over this range of length and time scale within a single simulation.

A promising strategy to advance fundamental combustion science is to develop a highly integrated effort that combines detailed scientific simulations with state-of-the-art experimentation. Experiments and computations that illuminate the phenomena at each scale are needed to develop computationally efficient models of the dominant behaviors at each scale. These models can then serve as the building blocks of simulations and experiments at successively larger scales.

Processes at disparate scales are not as easily partitioned as this picture suggests, raising critical fundamental scientific issues. The ultimate product of such research would be a set of mathematical models representing key combustion phenomena and their interactions. These models can serve as the basis of a new engineering design paradigm that would shift the focus of technology development from slow, costly prototype construction and testing to efficient, accurate computational design iteration and testing of proposed hardware designs.

Ultimately, reaching the goal of a predictive capability for comprehensive, device-scale combustion simulations will require coordinated research covering the entire range of combustion length and time scales. Specific needs include: (1) Theoretical methods to predict the pressure and temperature-dependent rates of multistep complex reactions, as well as detailed measurements of key individual reactions in order to verify and validate these computational tools; (2) efficient tools to generate complete combustion chemical mechanisms and tools for producing appropriate reduced mechanisms required for modeling macroscopic combustion systems; (3) experimental combustion diagnostics for nonintrusive, spatially and temporally resolved measurements of the concentrations and concentration-gradients of multiple species, temperature, radiation flux, and fluid velocities, typically required for benchmarking and validation of combustion simulations; and (4) high-fidelity numerical simulations of building-block flows that reveal fundamental turbulence-chemistry interactions in combustion. These physical and numerical experiments must be carried out at multiple levels of complexity. In particular, carefully executed benchmarks that are designed to expose or emphasize the role of particular physical subprocesses are required to assure that our scientific understanding is complete. Also, quantitative computational data and experimental measurements in device

environments are required to validate the capabilities of device-scale simulations to predict the complex interplay among the many important physical processes over a parameter space that enables the design of future combustion technologies. Figure 1-2 shows the necessary range of computations and experiments required to understand combustion.

The rich nature of the scientific challenge and its connections to combustion technology are illustrated by three example problems:

- soot formation in combustion systems and its coupling to other phenomena;
- the coupling of autoignition kinetics with turbulent mixing, enabling novel control techniques for homogeneous charge compression ignition (HCCI) combustion; and
- extensions of lean-limit combustion via hydrogen fuel blending.

Understanding the inception, growth, transport, and oxidation of soot is vital to controlling particulate emissions from diesel automobile engines, and soot radiative properties are central to heat transfer in boilers and furnaces. The gas-phase chemistry leading to soot formation involves hundreds of species and thousands of chemical reactions. New theoretical and experimental tools and techniques will be needed to elucidate the complex soot-formation chemistry. New theoretical methods are needed to rapidly and accurately predict the pressure and temperature dependent rate constants required to describe the early, rate-limiting steps of soot formation. The thermally-driven ordering of the initially disordered solid particle involves too many atoms for fully detailed simulation, so a reduced description of atom-atom interactions will be needed in simulations of this process. The clumping of soot particles to form wispy aggregates

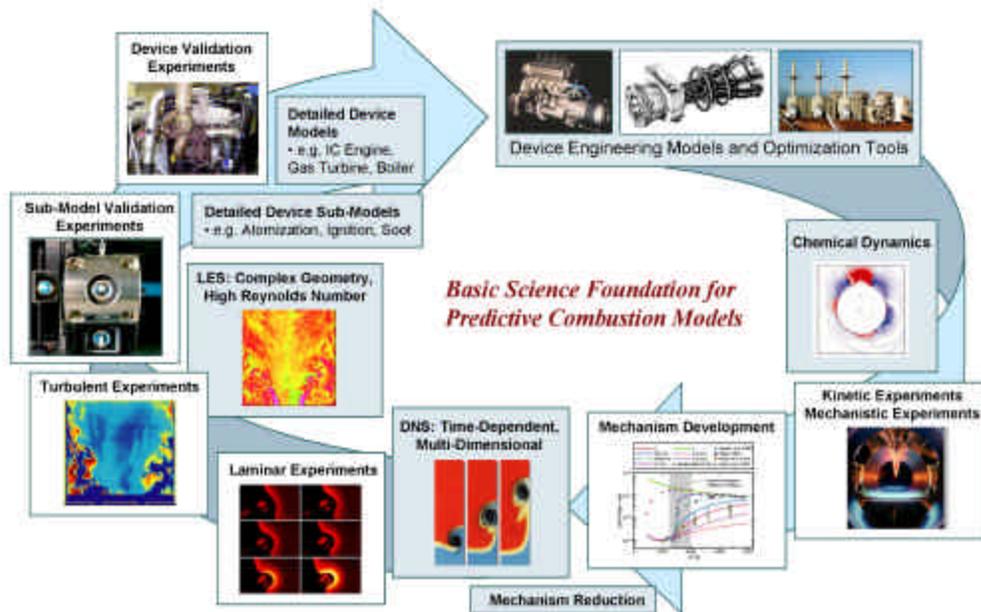


Figure 1-2. Applications of simulation tools and experimental capabilities designed to address combustion science.

cannot affordably incorporate atomic-scale processes, but the knowledge gained from finer-scale simulations will provide adequate surrogate representations. Heterogeneous chemistry experiments will be required to guide and validate model development. New experimental methods will be needed to quantify soot and soot precursors concentrations and morphology in combustion environments. The key role of soot as an absorber and emitter of radiation will be addressed computationally in a simulation that keeps track of the number and mass density of soot aggregates as they are transported through a combustor by turbulent fluid motions. Individual aggregates will not be resolved at this level of simulation. Other soot-related phenomena that will be studied computationally include autoignition and flame stabilization in a turbulent jet to determine the initial distribution of soot precursors, heat exchange between soot and nearby flames, turbulent mixing of soot-bearing gas with surrounding air, and oxidative destruction of the soot.

Homogeneous charge compression ignition (HCCI) combustion is an alternative engine combustion process that can provide high diesel-like efficiencies, while producing ultra-low NO_x and particulate emissions. Unlike a conventional spark-ignited engine, combustion occurs volumetrically^x throughout the cylinder as the charge is compressed, rather than in a flame front. This permits HCCI combustion to occur at relatively low temperatures, and therefore, dramatically reduce NO_x emissions. There are several outstanding technical barriers that must be overcome before HCCI can be widely^x applied to transportation engines. Fundamental research is required to control ignition timing and to limit the rate of combustion heat release to allow high-load operation. Overcoming these challenges requires an improved understanding of the close coupling between turbulent mixing and local chemical-kinetic reaction rates related to autoignition of large hydrocarbon fuels. This chemistry is the same as the chemistry associated with knock in spark-ignited engines. Turbulent mixing is thought to play a major role in mixture preparation and modulation of ignition kinetics. The inclusion of detailed chemistry in turbulent models is often impractical and methods for producing high-fidelity reduced mechanisms must be developed. Within practical engines, complete charge homogeneity is unattainable. An important research question is how mixing strategies lead to varying inhomogeneities in the charge, and how these inhomogeneities can be used ultimately to control the heat release rate, emissions and ignition timing.

Ultra-lean premixed hydrocarbon combustion (LPC) is currently one of the most promising concepts for substantial reduction of emissions while maintaining high efficiency. This mode of combustion is operated with excess air to reduce the flame temperature to levels that virtually eliminate NO_x production. Operating at the lean flammability limit poses significant challenges with flame stability, noise^x, and system dynamic responses. Minor fluctuations in the fuel/air ratio, for example, can lead to flame blowout, combustion instabilities, autoignition and flashback. Moreover, the intrinsic problems described above are compounded at high pressures. Understanding and controlling these phenomena is extremely important for the design of LPC stationary gas turbines and burners. Recently, hydrogen-enriched hydrocarbon fuels are being considered to improve flame stability characteristics during lean combustion. Hydrogen-enriched fuels modify both the flame structure and propagation aspects. Fundamental research is needed to characterize the behavior of combustion of enriched fuels. In addition to potential operational advantages, the development of hydrogen and hydrogen-blended hydrocarbon fuels for gas turbine applications will boost the use of alternative fuels. In the long term, these “designer” fuels will serve in the transition to a carbon-free fuel economy.

Such challenges will require multidisciplinary teams of computational and experimental physicists and chemists with access to terascale computer systems, state-of-the-art numerical algorithms, the latest advances in

computational science, and advanced optical diagnostics in modern experimental facilities. Significant new efforts are needed to describe heterogeneous processes, such as soot growth, and the effects of high pressure, for example in HCCI and LPC devices.

New Scientific Opportunities

Terascale computer systems and advanced experimental capabilities for combustion science offer unprecedented opportunities of synergistic, high-fidelity investigation of combustion phenomena. Direct Numerical Simulation (DNS) and high-fidelity Large Eddy Simulation (LES) methods are on the verge of becoming tools for fundamental investigation of the fully coupled dynamic behavior of reacting flows with detailed chemistry and realistic levels of turbulence. Information from such simulations, combined with detailed laser-based experiments on well-defined benchmark flames, present new opportunities to understand the central physics of flow/flame interaction and develop accurate, physics-based models for turbulent combustion.

Relevance and Potential Impact

Combustion of fossil fuels is the dominant mode of energy conversion, both nationally and globally, and it will remain dominant for decades. The truly predictive computational tools needed to effectively develop new combustion technologies with higher efficiency and lower emissions do not exist today. A focused BES effort dedicated to solving relevant combustion science problems will enable, for the first time, high-fidelity, fully predictive simulation of the next generation of combustion devices. Predictive capability will revolutionize the development process for advanced combustion technologies for transportation, power generation, and industrial processes, and it will greatly accelerate the global implementation of high-efficiency, low-emission systems. Fundamental advances in the science and modeling of chemically reacting flows will also have significant impact in chemical process engineering and atmospheric science.

Estimated Time Scale

The development of predictive simulation capability, which is applicable to a broad range of combustion problems, is a long-term goal. Substantial progress in the development of predictive models for the coupling of turbulence and chemistry in complex combustion systems can be expected within the next 5-10 years under the proposed program. Extension to prediction of complex phenomena, such as autoignition in turbulent heterogeneous mixtures or soot formation in combustion systems, is likely to require sustained effort over a 10-20 year period.

Nuclear Fission Energy

Materials Degradation

**Advanced Actinide and Fission Product
Separations and Extraction**

Fuels Research

Fundamental Research in Heat Transfer and Fluid Flow

MATERIALS DEGRADATION

EXECUTIVE SUMMARY

Future nuclear energy systems will need to provide (1) manageable nuclear waste, effective fuel utilization, and increased environmental benefits, (2) competitive economics, (3) recognized safety performance, and (4) secure nuclear energy systems and nuclear materials. Steady-state coolant temperatures in proposed next-generation reactor concepts range from 370°C to 1000°C, with projected accident transients that could reach temperatures to 1800°C for a short duration. These concepts involve exotic coolants such as lead-bismuth, lead, molten salt, or supercritical water. They must also perform satisfactorily while being subject to neutron damage levels greater than those experienced in any material developed for nuclear systems use to date. These expectations are unprecedented in nuclear energy or any other application and will require the development of a significant fundamental level of knowledge to successfully guide system development. In addition, information on materials performance in harsh nuclear environments is required to enable predictive modeling of material behavior in nuclear waste packages and other nuclear energy systems, such as accelerator-driven nuclear fission and transmutation. Opportunities for radical advances in fundamental understanding of the multiscale mechanisms and processes governing materials degradation are becoming possible through new and emerging advanced scientific facilities and high-performance parallel computing platforms. Integration of novel in situ experiments with theoretical/computational efforts provide the possibility to develop fundamental understanding of degradation mechanisms and kinetics over multiple scales, from atomistic to micron and nanosecond to minutes.

There is insufficient fundamental understanding of radiation effects on materials in nuclear reactor components to reliably predict component properties and thus mitigate service failures. The degradation of core components, including component welds and joints, and cladding in current and future nuclear reactor designs can lead to failures at high levels of neutron irradiation in the reactor coolant environment. The coolant chemistries (e.g., water, supercritical water, liquid metals) can become more aggressive in crevice situations, where component failures are often observed. Since cracking susceptibility requires a combination of radiation, stress and a corrosive environment, the failure mechanism has been termed irradiation-assisted stress-corrosion cracking (IASCC) for water coolants, but similar processes may occur in other coolant environments. Because testing of irradiated materials is difficult and expensive, it is highly unlikely that a purely empirical approach will provide an adequate understanding of corrosion processes. Much of this issue is tied to the co-evolution of equilibrium and non-equilibrium nanostructures and nanochemistries.

Research related to improved storage of spent nuclear fuels is another area of opportunity because there have been very few scientific studies on the behavior of nuclear waste packages. Qualification of new materials for nuclear waste packages needs to be scientifically based. This is critical in the absence of sufficient testing capabilities. Opportunities exist for major advances in this area through new and emerging in-situ experimental and diagnostic capabilities and parallel computational platforms. The properties of the spent nuclear fuel, other solid nuclear waste forms, the storage canister, and the drip shield may degrade in the presence of water, oxidizing environment, and radiation-induced chemistry changes (e.g., radiolysis, radioactive decay products). The fuel or waste forms are also subject to self-radiation-induced degradation from the decay of the radionuclides. This corrosion and radiation damage must be understood well enough that extrapolations of waste package behavior can be made confidently over periods of at least ten thousand years.

Summary of Research Direction

Advancing the fundamental mechanistic understanding of radiation-induced materials degradation to enable the predictive modeling of materials performance in the hostile environments (extremes of radiation field, temperature, stress, thermal/mechanical cycling, corrosive coolants, and oxidizing environments) associated with nuclear waste packages, nuclear reactors, and other nuclear energy systems.

New Scientific Opportunities

The DOE's Office of Nuclear Energy, Science, and Technology (NE), in conjunction with the ten countries that compose the Generation-IV International Forum (GIF), has been investigating nuclear reactor concepts that will be safer, more environmentally benign, longer operating, better performing and economically superior to current designs. The evaluation has included radioactive waste containment systems with the goal of generally optimizing the entire nuclear fuel cycle. This group has recently selected six nuclear reactor concepts for further R&D. The concepts are the Supercritical Water-Cooled Reactor (SCWR), the Very High Temperature (gas-cooled) Reactor (VHTR), the Gas-cooled Fast Reactor (GFR), the Lead-cooled Fast Reactor (LFR), the Sodium-cooled Fast Reactor (SFR), and the Molten Salt Reactor (MSR). The GIF expects the development of these concepts to occur over a 20-30 year time frame. A key to the success of all six concepts is improved structural materials to optimize economic performance and minimize the environmental impact of discharged waste.

There have been continued, but limited, studies of degradation of metal alloys for nuclear reactor components. The major scientific challenge in this area is the co-evolution of all microstructure components and their role in macroscopic material response such as swelling, anisotropic growth, irradiation creep, and radiation-induced phase transformations. Under irradiation the evolution of the microstructure is determined by the dynamic and kinetic response of a complex materials system when driven far from thermodynamic equilibrium. The detailed kinetic processes are both deterministic and stochastic, are coupled, and may evolve into new kinetic processes as the microstructure and phase transformation of the system evolves. The framework for this new era of radiation effects research should be the science of complex systems. While this emerging field is still in its definition phase, the needed understanding for radiation effects in solids provides a well-defined problem. It may, in fact, serve as a prime example or model of a complex system evolving in response to the continuous flow of energy that maintains the system in various states of non-equilibrium.

There is insufficient fundamental understanding of radiation effects on the chemical behavior of nuclear reactor components to reliably predict component properties and thus mitigate service failures. The degradation of core components, including component welds and joints, and cladding in current and future nuclear reactor designs can lead to failures at high levels of neutron irradiation in the reactor coolant environment. The coolant chemistries can become more aggressive in crevice situations, where component failures are often observed. Since cracking susceptibility requires a combination of radiation, stress and a corrosive environment, the failure mechanism has been termed IASCC. Because testing of irradiated materials is difficult and expensive, it is highly unlikely that a purely empirical approach will provide an adequate understanding of IASCC behavior. Much of this issue is tied to the co-evolution of equilibrium and non-equilibrium nanostructures and nanochemistries. Fundamental understanding of IASCC requires mechanistic research and novel approaches to examine reaction thermodynamics and kinetics at surfaces and crack tips. New results show crack-tip openings on the order of nanometers and corrosion/oxidation

fronts progressing with solution access through nanometer-size pores. Solution migration, electrochemistry and reaction phase stabilities need to be understood in the constrained dimensions and related to mechanisms controlling the propagation of environmental degradation. Mechanistic understanding of grain-boundary characteristics that control susceptibility of alloys to IASCC remain elusive. Degradation of welds and joints in nuclear components can lead to catastrophic failures, yet there is a critical lack of mechanistic understanding regarding weld microstructures and microchemistries. While there has been some progress in understanding these phenomena for water coolants, the behavior in supercritical water or other coolants is largely unknown. Much less is known regarding environmental degradation in high-temperature reactor systems, where refractory materials, including composites and ceramics, may be employed with gas coolants.

Ceramics are often more robust in durability and corrosion resistance, which is why they have often been proposed for the immobilization of actinides and other partition radionuclides. While ceramic nuclear fuels are currently used in nuclear reactors, future reactors could employ more ceramic composite components, such as in cladding and coatings for nuclear fuel. Advanced computational methods are required to understand, simulate and model the fundamental mechanisms that control the dynamics of radiation effects, diffusion and microstructure evolution in oxide ceramics, as well as at ceramic-ceramic interfaces, in radiation environments over broad ranges of temperatures. In oxide materials, both electronic excitation and elastic collision processes must be rigorously considered, unlike metals and semiconductors where electronic excitations play a lesser role. The critical problem is that the methodologies to perform accurate and reliable computations of radiation-damage processes in oxide ceramics over atomic to macroscopic scales are not currently available within the U.S. or elsewhere. The goal should be to establish a suite of computational methods that can perform modeling of oxide ceramics from the atomic to macroscopic scales on a level equivalent to or exceeding that performed today on metals and semiconductors. This goal is complicated by the mixed bonding character (ionic and covalent) and long-lived electronic excitations that are present in oxide ceramics. Achieving this goal requires development of novel simulation methods, potentials for complex systems, methods to handle complex potentials in parallel computing environments, and integration of electronic coordinates into potential models to implement charge-transfer and electronic excitations within large-scale ionic molecular dynamics (MD) simulations.

The nuclear waste packages for permanent disposition in the oxidizing environment of Yucca Mountain repository in Nevada are currently envisioned as consisting of spent nuclear fuel assemblies (or other solid nuclear waste forms proposed for future fuel cycles) that are contained in metal canisters that may be capped with a drip shield when finally emplaced in the repository. The properties of the spent nuclear fuel, other solid nuclear waste forms, the canister, and the drip shield may degrade in the presence of water, oxidizing environment, and radiation-induced chemistry changes (e.g., radiolysis, radioactive decay products). The spent nuclear fuel or solid nuclear waste forms are also subject to self-radiation-induced degradation from alpha and beta decay of the radionuclides. The environmental degradation due to corrosion and radiation damage must be understood well enough that extrapolations of waste package behavior can be made confidently over periods of at least 10,000 years. Public acceptance of nuclear power as an important energy source depends on developing acceptable solutions to the back end of the nuclear fuel cycle. Scientifically based and carefully engineered solutions are more likely to gain public acceptance.

Many previous models of nuclear fuels and component behavior in current reactors have been semi-empirical in nature and based on large and often incomplete databases. Predicting the performance of new materials for advanced reactor environments and nuclear waste packages in repositories is beyond the

capability of current models and databases. Opportunities exist for coupling experimental efforts and multiscale computational approaches to develop new materials and predictive performance models. Realizing this vision requires a large number of fundamental studies, including investigations of

- the thermal and radiation stability of nanometer oxide dispersion strengthened alloys;
- the dislocation interactions and strengthening mechanisms of radiation generated obstacles (voids, stacking fault tetrahedra, dislocation loops, etc.) and oxide precipitates that control plasticity;
- the controlling mechanisms of thermal and irradiation creep, creep cavitation and failure;
- the limited uniform ductility and flow localization at intermediate to low temperatures;
- the ability of nuclear waste packages to achieve long term (centuries) stability; and
- other dimensional effects such as swelling, phase transformations, and amorphization.

Other needs include:

- development of multiscale computational approaches;
- development of new radiation-tolerant materials (e.g., functionally graded, multilayer structures, composites, tailored nanostructures);
- development of a fundamental understanding of intergranular cracking in irradiated components; and
- multiscale modeling of the complex microstructural development of alloys and the relationship of these highly non-equilibrium changes to mechanical, dimensional stability, and corrosion properties.

Relevance and Potential Impact

Although radiation-induced materials degradation is not a new topic, opportunities for revolutionary advances in fundamental understanding of the mechanisms governing materials degradation over multiple length and temporal scales are becoming possible through new and emerging advanced scientific facilities and high-performance parallel-computing platforms. Novel in-situ experiments in realistic environments can be closely integrated with theoretical/computational efforts to develop a fundamental understanding of degradation mechanisms and kinetics over multiple scales from atomistic to micron and nanosecond to minutes. Such advances in this area will provide the underpinning science that will enable licensing nuclear waste packages for emplacement in the Yucca Mountain repository and the development and qualification of new materials for use within Generation-IV nuclear reactors and other nuclear energy systems, such as accelerator-driven nuclear fission and transmutation. In addition, the tools and methods developed in this effort will have a significant impact in the broader field of materials science.

Estimated Time Scale

Anticipated research program duration is 10-20 years.

ADVANCED ACTINIDE AND FISSION PRODUCT SEPARATIONS AND EXTRACTION

EXECUTIVE SUMMARY

Splitting atoms supplies energy to the nation from a uranium isotope that is less than 1% abundant in natural uranium. Ensuring an adequate long-term supply of fissile material is essential to maintaining or increasing electric energy generation using nuclear power reactors. At present world consumption rates, known uranium resources should last for about 65 years without recycling of spent reactor fuel. It is estimated that as yet undiscovered, but recoverable, uranium resources are at least four times larger than known uranium resources. Vastly larger amounts of uranium are present in seawater, although is not currently economically practical to recover such uranium. Energy production using nuclear fission has used two concepts for the final end point: (1) the “once-through” fuel cycle, in which spent nuclear fuel is planned to go directly to a repository, and (2) the “closed fuel cycle,” in which the spent nuclear fuel is reprocessed, with the separated uranium and plutonium going back for use in further fuel and the fission products planned to go to a repository.

Generation-IV reactor concepts are being designed to include reprocessing in order to extract a greater fraction of the energy content of natural uranium and thorium than is achieved currently. Thorium is more abundant in nature than is uranium and, like natural uranium, upon neutron bombardment is converted into fissile material that fissions to a degree as it builds up. By absorbing neutrons, the resulting fission products reduce the efficiency with which new fissile material is created. For this reason, actinide and fission product separation processing with recycling of the fissile isotopes to reactor fuel is being examined for full utilization of the energy content of present actinide resources as well as to minimize the volume of produced waste products. The present roadmap for advanced nuclear fuel cycles suggests that molten salt media may play an important role in the future. Improving separations efficiency is a viability issue for such media and should be addressed in basic research on the fundamental chemistry of thorium, uranium, selected transuranic elements, and salt-forming fission products in molten salt media. Studies under unusual or extreme oxidation and reduction conditions are needed also because little information is presently available under these conditions that may be encountered during a process upset or an accident scenario.

Achieving “green chemistry” is a goal worth establishing in separation processing of actinides and fission products. The term “green chemistry” is defined by the U.S. Environmental Protection Agency, in part, as the promotion of innovative chemical technologies that minimize the use of hazardous substances in the manufacture of chemical products. One step toward that goal is the replacement of presently used organic solvents with less hazardous liquids such as room-temperature ionic liquids (RTIL’s). The timeframe for maximum impact of fundamental studies on RTIL’s and molten salt media to be used is 10-20 years, when the results of such investigations must be factored into plant design decisions.

Innovative methods for recovery of uranium from seawater should be investigated if significant improvement over existing recovery techniques seems achievable. Deliberately designed ligands, perhaps analogues of the very specific ion channels of biological membranes or carbon nanotubes of appropriate radius whose specificity has been enhanced by modification of their interior surface or appropriate decoration of their entrances and exits with specific ion attracting functionalities, provide promising avenues to

achieve the required breakthroughs. Economic recovery of uranium from seawater is likely to be an issue in about 50 years.

Proposed Research Direction

Create the fundamental research basis for advanced actinide and fission product separation and novel extraction processes that are essential to ensure sufficient fissile material stocks, reduce costs, achieve proliferation resistance, and minimize environmental impacts and waste repository requirements in the nuclear fuel cycle.

New Scientific Opportunities

Ensuring an adequate long-term supply of fissile material for the nuclear fuel cycle is essential to maintaining or increasing the energy supplied to the nation by nuclear fission. About 0.7% of natural uranium is the fissile isotope U-235. Uranium is about as abundant on earth as are zinc or tin and is found at trace levels in most rocks and soils. Uranium is present in seawater to about 3 parts per billion. At present world consumption rates, the International Symposium on the Uranium Production Cycle and the Environment, held October 2-6, 2000 at the International Atomic Energy Agency (IAEA) in Vienna, concluded that the known uranium resources of 4 million tons (Mt) should last for about 65 years without recycling of spent nuclear reactor fuel. In addition, there are estimates of as yet undiscovered uranium resources of about 16 Mt in ore bodies, although recovery of that uranium is likely to be difficult. By some estimates, recovery of uranium from seawater using present technology would become economical if the price of uranium rose ten-fold.

Generation-IV reactor concepts provide opportunities both for reducing the radiotoxicity of non-fissile isotopes in presently stored spent reactor fuel and for creating new fissile isotopes. Recycling fissile isotopes provides a means of extracting a greater fraction of the energy content of natural uranium and thorium than is achieved in the current “once through” nuclear fuel cycle. Natural thorium is considered to be a “fertile feedstock,” meaning that its neutron irradiation results in the formation of fissile isotope U-233. Thorium is even more abundant in nature than is uranium, and generally thorium is less soluble in ground water or seawater due to its preference for the tetravalent state. If fissile isotopes are produced by neutron bombardment of natural or depleted uranium or natural thorium targets in nuclear reactors or in accelerator-based subcritical assemblies, utilization of nearly the full energy content of present uranium or thorium resources can be achieved. Irradiating such targets creates fissile isotopes that, as they build up, also fission to a degree. Such fission releases useful energy but also creates fission products, some of which strongly absorb neutrons. To achieve optimum neutron economy, actinide and fission product separation processing with recycling of the actinides to targets or reactor fuel is essential to maximize utilization of the energy content of present fissile and fertile actinide resources.

Some existing actinide processing is carried out in molten salt media, such the LiCl-KCl eutectic. The present roadmap of advanced fuel-cycle concepts suggests that molten salt media may play a significantly more important role in future actinide and fission product separation techniques due to the radiation resistance of such media. The fundamental chemistry of thorium, uranium, selected transuranic elements, and salt-forming fission products should be investigated in molten salt media because improving separations efficiency is a viability issue for such media. Investigations under unusual or extreme chemical oxidation and reduction conditions are necessary because little information is presently available on molten salt separations processes under these conditions. Examples of such conditions include molten salt that con-

tains high concentrations of elemental lithium or a transuranic element in metallic form, molten salt that is being sparged with chlorine gas, and molten salt exposed to nitrogen, oxygen, water vapor, or carbon dioxide (i.e., the potentially reactive constituents of atmospheric air), as might occur in an accident scenario. The timeframe for maximum impact of fundamental studies on molten salt separations processing is 10-20 years when the results of such investigations must be factored into plant design decisions.

Green chemistry is defined by the U.S. Environmental Protection Agency (EPA) as the promotion of innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. One highly promising approach to achieving “green chemistry” in separation processing of actinides and fission products is the replacement of organic solvents with less hazardous liquids. Certain mixtures of organic cations, such as methyl imidazolium derivatives, and charge-balancing inorganic anions of low complexing ability, such as triflates or hexafluorophosphate, form liquid phases at ambient temperature that are termed room temperature ionic liquids (RTIL’s) (e.g., see Figure 2-1). Only a minuscule fraction of compounds with potential to form such liquid phases have been investigated for their ability to form RTIL’s with useful properties.

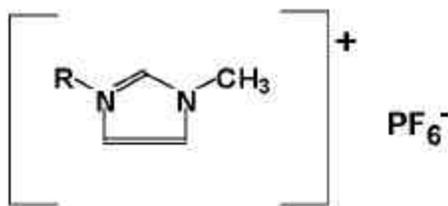


Figure 2-1. Generic structure of the room temperature ionic liquid alkylmethylimidazolium hexafluorophosphate, where **R** is an alkyl group.

Because the constituents of these RTIL’s are ions, no volatile organic carbon (VOC) is released during their use. The plutonium uranium extraction (PUREX) process used in most present aqueous-based separations processing of spent nuclear fuel relies on solvent extraction processing. In PUREX, some metal ions are extracted from an aqueous solution of nitric acid into an organic phase that is a mixture of alkane hydrocarbons (kerosene) and tributyl phosphate. The PUREX process emits both VOC’s and nitrogen oxides. A simplified version of PUREX, termed the UREX process, is the reference head end aqueous separations process for some Generation-IV nuclear reactor cycles. UREX also will emit VOC’s and nitrogen oxides. Although direct substitution of an RTIL for kerosene in PUREX or UREX processing is unlikely to be productive, novel extractant molecules, especially designed for use in an RTIL, hold significant promise for achieving superior performance. Some known RTIL’s have liquid ranges that exceed 300°C. Some are miscible with water or supercritical fluid (SCF) carbon dioxide; others are water- or SCF carbon dioxide-immiscible. A few RTIL’s have exceptionally large electrochemical potential windows, with one having been shown recently to allow electrodeposition of uranium metal. For this reason, selected RTIL’s should be investigated as potential replacements for high-temperature molten salts that are the basis for present pyrochemical and electrometallurgical processing of actinides. The radiolytic stability of RTIL’s is an area that clearly merits early investigation. The timeframe for maximum impact of fundamental studies on RTIL’s is 10-20 years, when the results of such investigations must be factored into plant design decisions.

Given the amount of uranium in seawater, the development of innovative methods for its isolation presents a major challenge. Deliberate design of ligands, using approaches that combine molecular mechanics modeling with experimental verification, is a promising avenue for identifying extraction agents capable of

achieving the required breakthroughs. For this purpose, one can envision such molecules attached to solid supports to facilitate extraction and ease of separation from solution by filtration to provide the desired elements, such as uranium, in essentially pure form, when starting from highly dilute solutions. Utilization of synthetic analogues of the very specific ion channels of biological membranes (sodium versus potassium, for example), in which the analogues are embedded in artificial membranes, is a further promising area of investigation. The resulting channels might be stacked complexes of host molecules or be carbon nanotubes so constructed as to have a radius appropriate to the specific translocation across the membrane of particular hydrated ions. Such specificity might be enhanced by modification of the interior lining of the carbon nanotubes or by appropriate decoration of their entrances and exits to facilitate specific translocations.

In a device using biological membranes, a very dilute solution containing a mixture of metal ions, such as seawater, would pass through a network of these membranes with one type of pore in each region of the apparatus; that region would then specifically collect a particular ionic species. Such an apparatus could be used to selectively collect uranium, for example. The economic viability of this approach could be enhanced by concurrent ability to isolate other valuable elements and produce desalinated water. At the other end of the nuclear fuel cycle, such a device could be employed to separate most components of dissolved spent reactor fuel (e.g., a mixture of actinides and fission products) thereby recycling unspent fuel and concentrating the most noxious by-products. These proposals have significant precedence in the natural world (ion channels in neurons or the loops of Henle of the human kidney, for example). Economic recovery of uranium from seawater is likely to be an issue in about 50 years.

Relevance and Potential Impact

The separations and extraction concepts outlined above provide challenging areas for creative fundamental research to generate the scientific knowledge base for creating applications that have immense significance to the production of energy by nuclear fission and the efficient, environmentally-friendly, handling and minimization of resultant waste products. Improving the closed fuel cycle requires efficient and effective recycle of actinides, such as uranium, and significant reduction of waste destined for geologic repositories. Novel separations and extraction methods are essential to meet the possible future needs of the closed nuclear fuel cycle, but they must overcome the current formidable obstacle of not being economical. The complex nature of mixtures of actinides and fission products and resulting radiolysis render profoundly challenging the development of such separation and extraction methods for the nuclear fuel cycle.

Estimated Time Scale

Two timescales are relevant to this research effort: 10-20 years for separation-related studies (to impact plant design decisions) and 50 years for extraction processes that achieve economic recovery of uranium from seawater.

FUELS RESEARCH

EXECUTIVE SUMMARY

In order to play their essential role in meeting future energy needs, advanced nuclear energy systems will need to provide: (1) manageable levels of nuclear waste, effective fuel utilization, and increased environmental benefits, (2) competitive economics, (3) recognized safety performance, and (4) proliferation-resistant nuclear energy systems and nuclear materials. The DOE's NE represents the U.S. and has a lead role in the Generation-IV International Forum (GIF), a group of ten countries working together to develop nuclear energy systems that make improvements in each of these four areas. The Generation-IV program is designed to develop reactors that meet these criteria and could be deployed by 2030. The GIF has recently selected six concepts for further R&D. The concepts are the Supercritical Water-Cooled Reactor (SCWR), the Very High Temperature (gas-cooled) Reactor (VHTR), the Gas-cooled Fast Reactor (GFR), the Lead-cooled Fast Reactor (LFR), the Sodium-cooled Fast Reactor (SFR), and the Molten Salt Reactor (MSR).

The GIF has completed an R&D Roadmap that describes the key viability and performance issues for the development of the six reactor concepts. Advances in fuel performance, including fuels that recycle actinides, have been identified as critical to the success of each. These fuels must achieve long lifetime while operating at high temperature. Additionally, as part of another NE program, the Advanced Fuel Cycle Initiative (AFCI), the DOE is investigating accelerator-based options for transmuting long-lived nuclear waste. These accelerator-based systems will investigate "inert matrix" fuels that do not use uranium and therefore maximize the overall burn rate of long-lived actinides. Because the success of novel fuel types is key to the success of these systems, developing a mechanistic understanding of their properties is critical.

The advanced nuclear energy system initiatives require the development of non-traditional fuel types (including nitride, metallic, dispersion, and inert matrix), the incorporation of large quantities of plutonium and higher actinides, and the inclusion of embedded isotopically-tailored neutron absorbers (burnable poisons). Additionally, each of these fuel cycle advances must be accomplished in a way that maintains an inherent proliferation resistance within the complete nuclear fuel cycle. These requirements motivate the need for fundamental understanding of the chemistry of elements in nuclear fuels; the thermodynamic stability in oxidizing and reducing environments; the physical properties (e.g., density, microstructure and thermal conductivity); the processing techniques for the fabrication of fuels containing actinides, plutonium and burnable poisons; and the response to radiation.

Proposed Research Direction

Provide a fundamental understanding of the chemistry, physical properties, and processing in proposed novel fuel forms and compositions, including nitride, metallic, dispersion, and inert matrix (non-fertile) fuels.

New Scientific Opportunities

The majority of fuels used in current nuclear energy systems were developed during the 1950s through the 1970s. Since then many significant advances in the tools for analyzing material properties have been developed. In studying the fuels for these advanced systems, critical Basic Energy Science analytical tools

such as synchrotron light sources, advanced electron microscopes, advanced neutron scattering centers, and facilities for conducting advanced computation need to be applied to ensure the best scientific tools are used to identify fundamental mechanisms of degradation.

In general, a long-term program to develop fuels for deployment entails at least the following four activities:

- fabrication process development,
- property measurement and assessment,
- irradiation testing and safety demonstration, and
- modeling and predictive code development.

Each of these activities must be conducted while remembering the requirement that any new fuels developed must be compatible with the associated recycle process. Current reactor fuels are primarily oxides, while for the Generation-IV systems, novel fuel types such as nitride, metal and dispersion fuels have been proposed. For accelerator-based transmutation systems and some reactor systems, inert matrix (non-fertile) fuels have been proposed. For all of these fuels, much fundamental understanding is lacking. A key fundamental scientific objective is to establish the basis for understanding and predicting fuel behavior (i.e., changes in density, melting point, thermal conductivity, tensile strength, corrosion resistance) under the temperatures, stresses, and radiation fields in the reactor.

Potential research topics include:

- behavior of novel fuel forms exposed to harsh environments (high temperature, high levels of radiation, and stress). These fuels include nitride fuels, metallic fuels, dispersion fuel, and non-fertile (inert matrix) fuels;
- for fuels made from reprocessed materials, the influence of recycled products on fuel behavior, including radiation response; and
- multiscale modeling of fuel thermomechanical behavior.

Generation-IV goals and the transmutation objectives for the AFCI program will present challenging performance requirements for new fuel types. Therefore, improving and optimizing performance potential will require a sound understanding of the mechanisms that impact fuel behavior and, ultimately, fuel lifetime. Such understanding is typically attained through development of mechanistic models for key phenomena and demonstrated through incorporation of those models into validated fuel performance codes. However, establishing mechanistic models requires knowledge of fundamental thermophysical, physical, and mechanical properties. These properties will influence important phenomena such as fission gas retention and release, fuel swelling, irradiation growth, fuel cladding chemical and mechanical interactions, and transient response. In the past, many fuel development programs were limited to empirical approaches that did not have the benefit of knowledge of those properties (although such information was often obtained with continued research on the well-established fuel designs). However, the challenges for the current programs require a coordinated effort to determine key properties for the fuel types (i.e., forms and compositions) as an important contribution to the fuel development process.

Inert matrix fuels do not contain fertile materials (materials that breed additional fissile constituents), such as uranium-238 or thorium-232, which allow a maximum burn rate of higher actinides. Inert matrix fuels are typically proposed as multiphase materials consisting of yttria-stabilized zirconia (YSZ) or magnesium

spinel (MgAl_2O_4), which are chemically and thermodynamically stable and insoluble in nitric acids. Inert matrix fuels may require the inclusion of burnable poisons to improve the reactivity coefficient profile during its lifetime. Fundamental understanding of the thermodynamic stability, fuel performance (response to irradiation), and fission gas release are needed.

Modeling of fuel performance is critical to predicting operational lifetimes. On a fundamental level, this includes obtaining critical material parameters from first principles calculations. These parameters can then be used in higher-level models such as molecular dynamics, Monte Carlo, and rate theory to describe events that have both short and long time scales and small and large distance scales. The development of these multi-scale computational methods will be critical to obtaining the predictive capability that is needed to extrapolate beyond the available experimental data.

The overall impact of advanced, alternate fuels on a repository program is not clear, and the economics of transmutation and recycling are current obstacles to their use. However, actinide recycle incorporating a fast-spectrum reactor has been identified as a means to manage the disposition of transuranic isotopes, which have long half-lives and dominate the calculated long-term dose associated with releases from repositories such as Yucca Mountain in the U.S. The fast-spectrum Generation-IV concepts are to be designed to accommodate minor actinides in fuel or in special targets. An understanding of minor actinide-bearing fuel materials is not well established. Therefore, key properties, such as thermal conductivity, enthalpy, and melting temperatures must be determined and understood. Other intrinsic characteristics, such as interdiffusion of fuel constituents under temperature gradients and interdiffusion with cladding constituents, must also be understood. The addition of the minor actinides adds a new level of complexity to fuel performance beyond that of “fresh” fuels.

Relevance and Potential Impact

The program of research outlined would produce a broad spectrum of results directly relevant to the DOE NE Generation-IV and AFCI programs. Development of computational tools and methods would be of benefit to the larger materials science community.

Estimated Time Scale

This program is expected to require 10-20 years of research.

FUNDAMENTAL RESEARCH IN HEAT TRANSFER AND FLUID FLOW

EXECUTIVE SUMMARY

The transfer of heat and the flow of fluids are fundamental to understanding and predicting the design of all types of advanced devices ranging from heavy-vehicle engines to computer chips and nuclear reactors. All forms of energy conversion systems, both present and future, require higher temperatures to achieve greater efficiencies. A better fundamental understanding of the processes involved is a critical requirement for the achievement of higher performance and assured licensing. A complete comprehension of the mechanistic phenomena related to multiphase fluid flow and heat transfer is lacking and to date relies on empirically derived correlations to predict the nature of these phenomena. New heat-transfer materials involving nanostructures provide exciting opportunities to extend the properties and applications of these materials. While efforts are on-going in these areas, considerable impact can be obtained over the next 15 years as measurement techniques and computational capabilities both rapidly expand.

Summary of Research Direction

Continued progress on a fundamental understanding of the physics of heat-transfer and fluid-flow issues is of great importance to many different future energy conversion and delivery technologies including transportation, electricity production, and many others. This crosscutting fundamental research direction is of critical importance because a better understanding of the basic features on a molecular level may allow future systems designers to greatly extend new materials and processes to optimize their performance. It is of particular importance to nuclear energy technologies, especially with the development of Generation-IV concepts during the next two decades, that a fundamental understanding of heat transfer under varying conditions be developed in order to reduce the uncertainties associated with the performance and safety of these advanced reactor concepts. Both design performance and licensing issues are driven and determined by the accuracy and uncertainties associated with the analysis of heat transfer and fluid flows in nuclear systems.

Generation-IV reactor concepts include numerous heat-transfer and fluid-flow challenges due to the selection of coolant materials for these systems. Coolants chosen for Generation-IV technologies include liquid metals (lead, sodium, and lead-bismuth eutectics), gases (helium and carbon dioxide) and supercritical water. An advanced understanding of heat transfer and fluid flow that includes a fundamental understanding, even to the point of eliminating the use of correlations for heat transfer and fluid flow analysis, would be very beneficial.

Traditionally, fluid flow and heat transfer in engineering systems are modeled using empirically derived correlations that are often only reliably applied for prescribed conditions and materials. This expedient method allows accurate and currently acceptable results, but as the next generation reactor designs move forward these analyses would be significantly improved by a better fundamental understanding of the basic physics and science at a molecular and atomistic level. Recent and expected future accelerations in computing capabilities can be utilized to probe the fundamental mechanisms related to molecular interactions between fluids and solid materials. Better instrumentation and measurement techniques can be designed to collect more detailed information with respect to heat-transfer and fluid-flow properties to provide better data for these expanded computer codes.

New Scientific Opportunities

To eliminate use of engineering correlations, it is necessary to develop a first principles understanding of multiphase heat-transfer and fluid-flow mechanisms, including the behavior of fluids such as supercritical water, lead and lead-alloys, and molten salts. In addition, there is the need to develop an understanding of fluids with dispersed particles (i.e., nanofluid suspensions).

There are a number of recent advances in multiphase fluid flow and heat transfer. Two-phase fluids using various combinations, including liquid/vapor, liquid/solid, and vapor/solid, offer enhanced heat transfer and fluid flow properties that can be utilized in energy conversion systems designs. Boiling and condensation heat transfer have been utilized for many years without a complete fundamental understanding at the microscopic and molecular scales to enhance heat transfer and system capabilities. Recent developments in microscale probes and non-destructive measurement techniques coupled with advanced computing technology give rise to considerable optimism that better fundamental understanding can be developed in the near future in two-phase flows and boiling and condensation heat transfer.

The recent development of nanofluid suspensions appears to yield novel heat-transfer and fluid-flow properties that provide another exciting possibility for enhanced system performance through the use of new materials and properties. This new class of heat transfer fluids is manufactured by dispersing nanometer-size solid particles in traditional heat transfer fluids to increase thermal conductivity and heat transfer performance. Experiments conducted to date have found that the improvement in heat-transfer properties of several nanofluids is significantly better than that predicted by existing theory. This represents a fundamental discovery in basic heat transfer and considerably more work is required to fully understand the principals of operation and the fundamental physics that give these materials enhanced capabilities. Original efforts by Argonne National Laboratory are being extended through work with Valvoline, Inc.; Nanopowder Enterprises of Piscataway, N.J.; and through collaborations with Purdue University and Rensselaer Polytechnic Institute to investigate the heat-transfer mechanisms in nanofluids. Applications in heavy transportation vehicles, supercomputer circuits, high-power microwave tubes, and advanced nuclear reactors are possible.

Relevance and Potential Impact

A truly fundamental understanding of heat transfer and fluid flow is advantageous to all forms of energy conversion systems, both present and future. Research leading to a comprehensive understanding of multiphase flow and heat transfer at the mechanistic level would yield significant design benefits for all types of advanced devices ranging from heavy-vehicle engines to computer chips and nuclear reactors.

Estimated Time Scale

The necessary research effort is estimated to require 15-20 years.

Renewable and Solar Energy

To Displace Imported Petroleum by Increasing the Cost-Competitive Production of Fuels and Chemicals from Renewable Biomass by a Hundred Fold

Develop Methods for Solar Energy Conversion that Result in a Ten-to-Fifty Fold Decrease in the Cost-to-Efficiency Ratio for the Production of Fuels and Electricity

Develop the Knowledge Base to Enable Widespread Creation of Geothermal Reservoirs

Conversion of Solar, Wind, or Geothermal Energy into Stored Chemical Fuels

Advanced Materials for Renewable Energy Applications

TO DISPLACE IMPORTED PETROLEUM BY INCREASING THE COST-COMPETITIVE PRODUCTION OF FUELS AND CHEMICALS FROM RENEWABLE BIOMASS BY A HUNDRED FOLD*

EXECUTIVE SUMMARY

Emerging knowledge in functional genomics and molecular technologies provides new opportunities for the genetic tailoring of plants and microorganisms to produce novel materials, fuels, and chemicals. During the past century, plants have been extensively modified to vastly improve the production of food, feed, and fiber. An understanding of fundamental mechanisms that govern the physical limitations of plant efficiency will allow the design and control of many useful plant properties. These include the control and characterization of plant architecture and composition (lignin, cellulose, hemicellulose, starch, and oils), improvements in the energy efficiency of plant production (reduced nutrients, water, and land requirements), and an expansion in the range of environments that can be used for cultivation (salt tolerance and stress resistance). Further advances in the fractionation of biomass into individual components using physical and chemical treatments offer a major opportunity for cost savings. Metabolic engineering of new microbial biocatalysts offers the potential to produce novel biomaterials and chemicals that will serve as renewable alternatives to current petrochemicals. These improved microbial biocatalysts are required to expand the range of useful conditions for industrial fermentations and reduce costs through process simplification. Substantial cost savings can also be realized by the development of biocatalysts that produce enzymes (i.e., cellulase, xylanase, etc.) for carbohydrate depolymerization as coproducts during fermentation, eliminating the need for separate enzyme production facilities. Application of biochemical and genetic principles provide mechanisms for the rational design of improved enzymes concerned with the depolymerization of plant constituents. Recent expansion in genomic sequences from microbes and plants provides a vast toolkit of genes and enzymes that can now be recombined and used to provide clean and sustainable solutions to our current dependence on imported petroleum.

Summary of Research Direction

The modern industrial revolution has been powered by the use of solar energy from ancient plants and microalgae that formed vast deposits of petroleum, coal, and natural gas. The ancient photosynthetic processes that produced these reservoirs of fossil energy also shaped our climate and the composition of our atmosphere. Storage of carbon in relatively inert fossil forms reduced atmospheric carbon dioxide and other compounds associated with planetary heating and produced our oxygen-rich atmosphere. The vast scale of biological conversion processes offers the opportunity to replace part of our dependence on fossil residues for energy with contemporary sources of renewable biomass. Biological transformations of renewable biomass materials also offer the opportunity to displace current petroleum-based chemicals and plastics using environmentally friendly processes. Co-production of these higher value chemicals from renewable biomass is essential to reduce the cost of liquid fuels such as ethanol or biodiesel from biomass.

Approximately 0.2% of the current U.S. energy needs are supplied by renewable biomass, principally through direct combustion (heating or electricity) or ethanol as a fuel extender and oxygenate (providing 2

*This document served as the basis for a subsequent Proposed Research Direction from the Energy Biosciences Team entitled "Energy Biotechnology: Metabolic Engineering of Plants and Microbes for Renewable Production of Fuels and Chemicals."

billion gal/yr or 1.3% of total automotive fuel). Both the areas of liquid fuels (i.e., ethanol and biodiesel) and combustion offer tremendous opportunities for expansion through the development of improved methods for the solubilization of plant constituents and the application of our emerging knowledge of plant and microbial genomics.

Near term expansion of research should focus on the development of improved bioconversion processes to produce chemicals (e.g., ethanol, longer chain alcohols, fatty esters, etc.) that can be blended with currently used automotive fuels (i.e., gasoline and diesel) and on the development of microbial processes for higher value coproducts (i.e., commodity chemicals and bio-based plastics) that displace imported petroleum and increase revenues. Underutilized residues from current agriculture and forestry with little or no current value should be used as feedstocks for this near-term expansion. Approximately 30 million tons (Mt) of corn is currently converted to fuel ethanol in the U.S. by a mature industry using very efficient processes that take advantage of the highly digestible nature of starch by microbial enzymes. While this can continue to expand and make an important contribution to the energy security of our nation, the energy-intensive nature of corn farming and competing uses of corn as food and feed will prevent the substantial replacement of automotive fuel by ethanol from corn alone. In contrast, the use of undervalued lignocellulosic residues as feedstocks should have minimal impact on consumer costs for the primary products from agriculture (food, feed and fiber). This new use represents an expanded benefit with minimal investment of additional energy. Additional fuels from lignocellulosics can be blended with gasoline to reduce petroleum imports while maintaining the benefits of corn-based ethanol production.

The high capital cost and increased risk associated with process complexity have thus far blocked the industrial implementation of many promising new technologies. Much of this process complexity can be reduced through the genetic engineering of improved microbial biocatalysts, the genetic tailoring of the plants for specific applications, and by improvements in plant fractionation technologies that increase efficiency and reduce costs. Even with process simplifications, the barrier of risk associated with the first implementation of a novel technology should not be underestimated.

New Scientific Opportunities

Many aspects of process complexity can be improved by the application of knowledge from microbial and plant genomics. Genomic sequences provide a catalogue of genes that can be used to alter cellular structure, composition, and function. These sequences provide a starting point for our understanding of integrated processes that limit the efficiency of water and nutrient use, the partitioning of photosynthate among cellular constituents, tolerances to extreme environments, and bioconversion processes by microorganism. A logical next step is to expand these genetic catalogues by adding fundamental knowledge concerning the integration of gene functions and physiological activities.

Cellulose depolymerization by enzymes is arguably the single most expensive step associated with the bioconversion of lignocellulose to fuels and chemicals. Increased understanding of the molecular mechanism of glycohydrolases may lead to creation of more efficient enzymes that resist product inhibition. Additional approaches include the coproduction of glycohydrolases by the microbial biocatalysts during fermentation and the coproduction of glycohydrolases in the tissues of plants prior to harvesting for bioconversion. Significant reductions in added cellulase will also be achieved by improved understanding of the fundamental chemical and physical processes involved in the fractionation and solubilization of biomass.

Our increasing facility and knowledge of plants should also support a more radical approach to biomass feedstocks, the genetic tailoring of plant composition for specific bioconversion processes. Continuing investigations of fundamental mechanisms that regulate the partitioning of photosynthate between carbohydrate polymers (i.e., cellulose, hemicellulose, and starch), protein, lipid, and lignin should now allow rapid improvements in plant composition for fuels and chemicals equivalent to those that have been realized in food crops. For instance, increasing the lignin content with reduction in carbohydrate content would increase the energy density of plant residues intended for use in combustion. Alternatively, increasing the production of carbohydrate polymers that can be readily degraded by enzymes (i.e., starch and hemicellulose) and reducing the content of cellulose and lignin could eliminate the need for cellulase enzymes in bioconversion processes. Relatively small lignin and cellulose residues that remain after enzyme treatments of such materials could be burned to provide steam and power.

Broad implementation of biomass as a primary energy source in the U.S. and in the world will depend upon the genetic modification of plants to expand the range of soil environments for productive cultivation, to minimize nutrient requirements, and to increase crop productivity (tons/acre per year). These improved plants will become the feedstocks of the future. Areas of particular interest include salt tolerance, metal tolerance, and improved efficiencies for the use of water and nutrients. This is a longer term goal where sustained investment in fundamental research is essential. Again, the field of genomics provides a wealth of information by cataloguing the genes. However, continuing fundamental studies are essential to understand the mechanisms that have evolved to control these macro functions in plants and microorganisms. Results from these investigations will serve as a guide for the rational design of future improvements using both traditional and molecular approaches.

Relevance and Potential Impact

The efficiency with which we have converted fossil biological energy sources into fuels and chemicals has allowed a tremendous expansion in population and improvement in the quality of life throughout the industrialized world. As we look toward a future that must rely upon alternative energy sources, the same fundamental biological processes that created fossil deposits and our oxygen-rich atmosphere can be harnessed to provide a renewable source of energy and chemicals. Traditional plant breeding coupled with chemical and microbial conversion processes has allowed hundred- to thousand-fold increases in the production of food and food products over the past the century with small recent contributions from genomics and molecular methods.

Estimated Time Scale

These new methods, together with new advances in materials science and chemistry, offer the opportunity for even greater improvements in bio-based products over the next 50 years and provide the basis for the conservative estimate of a hundred-fold increase in contribution of renewable biomass (meeting 20% of the nation's energy needs) to our national security.

DEVELOP METHODS FOR SOLAR ENERGY CONVERSION THAT RESULT IN A TEN-TO-FIFTY FOLD DECREASE IN THE COST-TO-EFFICIENCY RATIO FOR THE PRODUCTION OF FUELS AND ELECTRICITY

EXECUTIVE SUMMARY

The grand challenge for solar energy utilization is to develop conversion systems that are stable and robust for a 20-30 year period and that result in a ten-to-fifty-fold decrease in the cost-to-efficiency ratio for the production of electricity and fuels. To reduce the cost of installed photovoltaic systems to \$0.20 per peak watt of solar radiation, a cost level that translates into \$0.01-\$0.02/kWh, or to reduce the cost of solar fuels to \$1.00/GJ, costs that would make solar photoconversion very attractive economically in today's energy market, will require truly disruptive technologies that do not exist at the present time.

To achieve low solar cost- to- power (electrical or chemical) ratios, at least three approaches are possible. In a first approach, chemical methods are needed to enable inexpensive photoconversion materials (like polycrystalline, nanocrystalline, and organic materials) to perform as if they were expensive single crystals. A second approach is to produce so-called interpenetrating networks. Such an approach relaxes the usual constraint in which the photogenerated carriers must exist for long enough times to traverse the entire distance of the cell and be efficiently separated and collected. Instead, the materials consist of a network of interpenetrating regions that facilitate effective charge separation and collection over very short distances. A third approach involves developing novel methods to obtain extremely high conversion efficiencies at modest cost. Present photon conversion devices based on a single threshold absorber and full thermal relaxation of the photogenerated carriers, including semiconductor photovoltaics, have a theoretical thermodynamic conversion efficiency of 32% in unconcentrated sunlight, but the conversion efficiency can be increased, in principle, to 45-65% if carrier thermalization can be prevented. Multiple bandgap absorbers in a cascaded junction configuration can offer high efficiencies, particularly when highly concentrated sunlight can be used, but the materials are expensive. Approaches to achieving high efficiencies at moderate materials cost might utilize semiconductor quantum dots, quantum wells, organic dyes, and related nanostructures. In either of the above approaches, the interfaces necessary to separate and collect the charge carriers can be formed using solids, liquids, or polymers, but the resulting photoconversion structures must be inexpensive and manufacturable on a large scale.

Summary of Research Direction

The efficiency of photovoltaic devices has been increasing steadily. Nevertheless, current technologies all lie on a relatively common cost/watt (W) scale. The underlying reason for this roughly equal cost/W trade-off is that the photovoltaic materials now available suffer from the same fundamental physical limitations. Large-grain pure materials, with a long lifetime capable of making efficient solar cells, are costly to produce. Alternatively, cheaper materials with smaller grain sizes have grain boundaries that act as recombination sites, resulting in inefficient solar cells. A similar trade-off is found for organic ("plastic") photovoltaics. If pure inorganic single-crystal materials, like silicon and GaAs, are replaced with much cheaper organic materials, the materials are inherently disordered and therefore are cheaper but more inefficient. The net result is that one can ride anywhere on this cost/W trade-off scale, but nevertheless end up at the same cost/W ratio to within a factor of 20%. To reduce the cost of photoconversion systems for the production of solar electricity to \$0.20/peak W of solar radiation and solar fuels to \$1.00/GJ cost levels that would make solar photoconversion very attractive economically in today's energy market, will require scientific breakthroughs and associated truly disruptive technologies that do not exist at the present time.

One important strategy to attain these goals is to identify approaches that produce ultrahigh conversion efficiency at modest cost. Present photon conversion devices based on a single threshold absorber, including solid-state semiconductor photovoltaics, all operate within a regime wherein the ultimate thermodynamic conversion efficiency is limited to about 32% with unconcentrated sunlight. In this regime, the photogenerated electrons and holes are in thermal equilibrium with the phonons (quantized lattice vibrations) of the light-absorbing material. This means that the energy of photogenerated electrons and holes in excess of the threshold energy (i.e., the bandgap) is not utilized for useful work, but rather is converted into heat. Furthermore, in this regime, photons less energetic than the threshold energy are not absorbed. Recent research has shown that the equilibration of electrons and phonons (also referred to as hot electron cooling) can be slowed by one to two orders of magnitude in semiconductor quantum dots, quantum wells, and related nanostructures. Thus, useful electrical or chemical work may possibly be extracted before thermalization occurs, resulting in higher conversion efficiencies. Other researchers have shown that conversion efficiencies above the 32% limit may also be achieved by: (1) the formation of resonant impurity bands in photoelectrodes produced from quantum dot solid arrays that can absorb two sub-bandgap photons to create one electron-hole pair; (2) photon up-conversion, whereby a higher energy photon is produced from two lower energy photons; and (3) photon down-conversion, whereby two smaller energy photons are produced from one energetic photon. Another approach to achieving high conversion efficiency, also yielding a theoretical thermodynamic maximum of about 65%, is to use multiple bandgap absorbers in a cascaded tandem configuration. In the limit of threshold absorbers matched to the solar spectrum the limit is 65%, but two tandem bandgaps are estimated to yield about 40% conversion and three tandem bandgaps to yield about 50% conversion.

Another approach to meet these cost/W goals is to find chemical methods to fool the inexpensive photoconversion materials (like polycrystalline, nanocrystalline, and organic materials) into performing as if they were expensive single crystals, without actually incurring the costs to grow the expensive crystals themselves. This approach involves chemically treating these inexpensive materials so as to fool their grain boundaries or interfaces into thinking they are part of the periodic crystal that this material is trying to emulate (e.g., see Figure 3-1). A related strategy is to produce so-called interpenetrating networks. Use of such networks relaxes the usual constraint in which the carriers that are excited must exist long enough in their excited states to traverse the entire distance of the cell. Instead, the materials consist of a network of interpenetrating regions. There are two examples of these approaches that are just emerging. Neither of them are economically or technologically viable today, but they seem like good approaches in the long run to achieve the difficult cost goals of #\$.01-\$.02/ kWh.

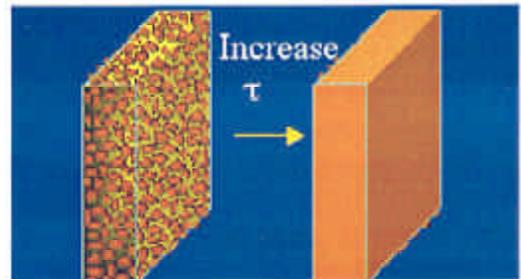


Figure 3-1. Solar paint passivates grain boundaries in inexpensive photovoltaics, causing them to perform like expensive single crystal materials.

New Scientific Opportunities

In either of the above approaches, the interfaces necessary to separate and collect the charge carriers can be formed using solids, liquids, or polymers. In any successful system, the resulting photo conversion structures must be inexpensive and manufacturable on a large scale. Photoelectrochemical cells, polymer/inorganic semiconductor junctions, thin-film photovoltaic materials deposited by chemical methods, and organic conductors and semiconductors are all possible materials that should be explored for this purpose.

An interesting feature of photoelectrochemical cells is that they are inherently more tolerant of grain boundary effects than solid-state systems and additionally such cells can be configured to store the photogenerated electricity by using part of the photogenerated power to charge a third electrode in the cell, which can discharge in the dark. Such a cell becomes a photochargeable battery that can deliver power day and night. In the end, regardless of which materials system is implemented in the conversion device, the fabrication and assembly of the conversion device will have to be as cheap as painting your house and will need to be mass produced as inexpensively as printing the daily newspaper or making photographic film.

Relevance and Potential Impact

Recent detailed analyses indicate that from 10-30 TW-yr of annual carbon-free energy will be required by the year 2050 to accommodate the world's expected population combined with a modest annual global economic growth rate of about 2%. The range of required carbon-free energy depends upon the level of atmospheric CO₂ that can be tolerated. About 10 TW-yr of carbon-free energy annually will be required to stabilize CO₂ at 750 ppm, while about 30 TW-yr annually will be required for stabilization at 400 ppm. The current atmospheric CO₂ level is 275 ppm, compared to 175 ppm before the industrial revolution. Today, the total annual consumption rate of energy is about 12 TW-yr. Thus intense energy research and development is required to enable the introduction of such large amounts of carbon-free energy into the world's energy infrastructure on this timescale.

The solar constant is 1.76×10^5 TW, which is much larger than the 12 TW mean global energy consumption rate from all sources at the present time. Hence, there is ample solar energy potential to provide all of our energy needs from a renewable, carbon-free power supply. From the 1.2×10^5 TW of solar energy that strikes the earth's surface, a practical siting-constrained terrestrial solar power potential value is about 600 TW. The numbers range from very conservative estimates of 50 TW to optimistic estimates of 1500 TW, depending on the land fraction devoted to power generation. A good number to use for onshore electricity generation potential is probably 600 TW. Thus, for a 10% efficient solar farm, at least 60 TW of power could be supplied from terrestrial solar energy resources. For calibration, photosynthesis currently supplies 90 TW globally to make the biosphere run, so the amount of power available from the sun is very large.

The land area that is required to produce 20 TW of carbon-free power from solar energy is 0.16% of the earth's surface, or 5×10^{11} m². Producing 3 TW (the current U.S. energy consumption rate from all sources) with 10% efficiency would require covering 1.7% of the land in the U.S., an area comparable to the land devoted to the nation's interstate highways.

Estimated Time Scale

10 Years

DEVELOP THE KNOWLEDGE BASE TO ENABLE WIDESPREAD CREATION OF GEOTHERMAL RESERVOIRS

EXECUTIVE SUMMARY

There is a critical need to significantly increase the power generating capacity globally over the next 50 years, while minimizing the environmental impact. The natural thermal gradient of the earth's crust represents an extensive global geothermal resource, limited only by our inability to tap the gradient by creating productive and sustainable geothermal reservoirs. For example, exploitation of the geothermal gradient in the western U.S. alone could add as much as 0.1 TW of base load electrical power. The extent to which this vast potential resource can contribute to increasing demand will depend on conceptual and technical advances related to the creation and sustainability of productive reservoirs, where natural permeability and/or fluid content are limited. To meet this goal, basic research on all aspects of fractures and fracture networks in competent crystalline rock will be required. Specific critical research areas include: (1) the need for reliable high-resolution techniques for remote fracture mapping, (2) coupling mechanical properties and the local state of stress of reservoir rocks to stimulated fracture geometry, (3) mechanical and chemical techniques for sustaining stimulated fracture permeability, (4) new techniques for quantitative assessment of the coupled thermal and chemical interaction of injected fluids with the stimulated reservoir fractures and reservoir matrix, (5) new materials and coatings to enable drilling and heat harvesting at temperatures above 300°C, (6) new sensor technologies that will work at these temperatures, and (7) the same technologies at temperatures from 500-1000°C.

Summary of Research Direction

Geothermal energy is derived from the inherent heat content of the earth's crust. Circulating groundwater mines the heat from hot crustal rocks and energy is extracted from the heated groundwater. With research support from the U.S. DOE, significant progress in defining U. S. geothermal resources has been made. Resources with obvious geothermal manifestations, such as geysers, hot springs, fumaroles, mud volcanoes, etc., have been developed or tested, and currently provide ~2800 MW_e of geothermally derived electricity. It is conceivable that improvements in exploration and production technologies could increase the output from natural systems by as much as a factor of ~2-10. However, given the predicted need for 10-30 TW of clean power by the mid-21st century, extensive technological advancements will be required if the vast geothermal energy potential of the earth is to be exploited and added to the global energy mix. To meet future demands, geothermal research should be directed at tapping the inherent heat of the earth's crust by creating engineered geothermal systems.

Past research efforts have demonstrated the technical feasibility of creating an engineered geothermal resource. However, no commercial systems have been constructed and there is no conclusive proof that productive sustainable reservoirs can be developed. Never-the-less, the vast energy potential represented by the earth's natural thermal gradient should be a resource target. Ideally, a successfully engineered system will be one in which the inlet and outlet conditions of fluid pressure, temperature, flow rate, and water chemistry can be constructed, manipulated and controlled. Engineered systems, like their natural counterparts, will likely be hosted in competent crystalline rocks, where fluid flow and heat exchange is fracture controlled.

New Scientific Opportunities

To meet this scientific challenge will require extensive basic research into the nature and all aspects of fractures, fractured rocks, and the interaction between the water circulating through the fractures and the heat contained in the matrix rock hosting the fractures. Specific critical research areas include: (1) the need for reliable high-resolution techniques for remote fracture mapping, (2) the ability to couple mechanical properties and the local state of stress of reservoir rocks to the stimulated fracture geometry, (3) the development of mechanical and chemical techniques for sustaining stimulated fracture permeability, (4) new techniques for quantitative assessment of the coupled thermal and chemical interaction of injected fluids with the stimulated reservoir fractures and reservoir matrix, and (5) extending drilling technologies to higher temperatures than presently accessible.

High resolution remote fracture mapping. Fundamental research in the area of subsurface imaging, with a focus on geophysical methods, will enable the development of technologies for remote fracture mapping. Seismic methods are obvious candidates, since it is known that fractures scatter seismic energy, cause mode conversions, and trap and guide seismic waves. Further work is needed to establish a more quantitative relationship between fracture properties of interest, such as length, connectivity, and permeability, and of changes in the wavefield. Further work is also required to establish quantitative attributes of the seismic signature typically measured in the field. Seismic amplitudes can be used if the relative contribution of scattering and intrinsic attenuation can be better understood, particularly under the multiphase chemically reactive environment of a geothermal reservoir.

Field application of seismic methods will involve deployment of surface and subsurface sources and receivers. In this regard, the huge amount of experience in the petroleum industry is not easily transferred to geothermal. There are few geothermal reservoirs located in sedimentary environments for which conventional acquisition strategies have been developed. Passive source concepts should be further explored, since it is known that geothermal production activities yield many microseismic events.

The difference in the geologic environments of petroleum and geothermal resources also means that data processing techniques from the petroleum industry are not easily adapted to geothermal applications. Fundamental research is needed to derive new algorithms for processing of the seismic wavefield generated in very heterogeneous strongly scattering media.

Other geophysical methods, such as electrical and electromagnetic, gravity, and surface deformation, are of lower resolution than seismic but potentially provide information to compliment seismic measurements. Further fundamental research on the effect of fractures on potential field measurements is needed.

Rock mechanical properties, local stress, and stimulated fracture geometry. The fundamentals of rock fracture have been studied extensively for 40 years. Nonetheless, the technology for fracture stimulation of geothermal reservoirs is not well defined, despite several field-scale attempts. Further fundamental research needs to be focused on understanding fracture initiation and propagation in rock in which there is a network of pre-existing fractures containing fluids of multiple phases subjected to large thermal and hydrologic pulses. The relative contribution of brittle and ductile processes needs to be studied for the hydrothermal conditions and rock types present in geothermal reservoirs. Though it is known that microseismic activity accompanies such stimulation processes, further research is needed to quantitatively interpret these events in terms of changes in hydraulic properties of the rock.

Sustaining stimulated fracture permeability. Experience in reservoir stimulation using such techniques as fluid acidification, injected propellants, hydro-fracturing, sand injection, etc. has demonstrated the feasibility of enhancing near-well bore permeability. Engineered geothermal systems introduce a new level of complexity, because permeability must be enhanced and sustained over the distance between an injector and production well and over long periods of time. Long-term success of an engineered system will require future research in physical and chemical methods for maintaining open fluid pathways.

Coupled thermal and chemical interaction between injected fluid and reservoir rock. The thermal power performance of an engineered reservoir will depend on the coupled efficiency of fluid circulation and heat extraction. Surface seismic methods can define a seismic reservoir volume. Conservative fluid tracers can map fracture connectivity between an injection and production well. However, there is no direct measurement that couples the seismic volume and fracture connectivity to the effective heat-transfer volume. The latter is a necessary parameter for understanding, modeling and predicting thermal power performance.

A major objective of future research should be to develop reliable techniques for determining the effective heat-transfer efficiency over an integrated fluid-flow path. Fundamental research is needed to develop the chemical, isotopic, and advanced microscopic techniques for geochemical characterization of fluid-rock systems from the microscopic, to the molecular, to the field scale. For instance, presently it is not well understood why fluid-rock reaction rates determined in laboratory-scale experiments are up to several orders of magnitude faster than similar reaction rates measured on a field scale. Of fundamental importance is the ability to model fluid transport, fluid-rock interaction, the rate and distance scales over which these processes occur, and an effective surface area of fluid-rock exchange.

High-temperature drilling technologies. In order to extend the geothermal resource potential to greater depths and higher temperatures, high-temperature drilling technologies will need to be advanced. Future research should focus on developing new materials and coatings to enable drilling and heat harvesting at temperatures above 300°C, new sensor technologies that will work at these temperatures, and the same technologies at temperatures from 500-1000°C.

Relevance and Potential Impact

The natural thermal gradient of the earth's crust is ~30-100°C/km and represents an extensive global geothermal resource of high potential. For instance, exploitation of the thermal gradient in the western U.S. alone could add as much as 0.1 TW of baseload electric power. Access to this resource is limited only by our present inability to tap the natural thermal gradient and create geothermal systems. To create a productive and sustainable geothermal power resource from the natural thermal gradient, the biggest scientific challenge will be engineering the appropriate mix of permeability, fluid pressure, water flux, and heat exchange. In most regions, adequate heat is accessible with present drilling technologies. Access to deeper and hotter systems, thus extending the geothermal resource, would require future advances in high-temperature drilling technology.

Estimated Time Scale

Initial goal is 0.02 TW of baseload electric energy from engineered systems by the year 2020. Secondary goal is 0.1 TW by the year 2040. Final goal is technological development for exploiting deeper hotter systems in regions of normal and higher than normal thermal gradients.

CONVERSION OF SOLAR, WIND, OR GEOTHERMAL ENERGY INTO STORED CHEMICAL FUELS

EXECUTIVE SUMMARY

In one approach, electricity would be produced by the conversion devices and then converted separately into storable fuels. For this approach to be cost-effective and energy efficient, new catalysts are needed to facilitate multi-electron transformations, such as evolving hydrogen and oxygen from water or reducing CO₂ to methanol, ethanol, or other carbon-based fuels. In a second approach, the fuel is made directly or in an integrated system with the energy conversion device. Direct solar photoconversion is the process whereby the energy of solar photons is converted directly into fuel starting from simple and renewable substrates, such as water, CO₂, and N₂. These processes require photoactive organic, inorganic, or biological molecules or materials that can absorb a large fraction of the solar irradiance and drive the chemical reactions that produce the fuels of interest.

Summary of Research Direction

Direct solar photoconversion is the process whereby the energy of solar photons is converted directly into fuels starting from simple and renewable substrates, such as water, CO₂, and N₂. These processes require photoactive organic, inorganic, or biological molecules that can absorb a large fraction of the solar irradiance and drive the chemical reactions that produce the fuels of interest. Direct formation of fuels will require development of inexpensive, robust, and efficient thermal and/or photochemical catalysts for the formation of such fuels from abundant, inexpensive, recyclable chemicals. Important targets include the direct photochemical splitting of water into H₂ and O₂; catalysts that could be used, either in an integrated fashion with photoelectrochemical devices or in a modular fashion with photovoltaic systems, and that individually reduce water to hydrogen and oxidize water to oxygen; and catalysts that effect the reduction of CO₂ to organic fuels (such as methanol or methane) or that utilize H₂ and CO₂ to form hydrocarbon fuels.

Three branches of science and technology can be defined for direct solar photoconversion: photoelectrochemistry, photochemistry, and photobiology. They all depend upon photo-induced charge generation (i.e., electrons and positive holes) followed by efficient positive and negative charge separation at various types of interfaces that ultimately produce oxidation-reduction (redox) chemistry. Photoelectrochemistry involves semiconductor-molecule interfaces, photochemistry involves molecule-molecule interfaces, and photobiology involves biological interfaces with other biological and non-biological molecules.

Fuels produced by solar photoconversion are derived from endoergic reactions wherein the photon energy is stored as chemical free energy in the reaction products. Extremely important examples of this process are hydrogen from photolytic water splitting and formation of methane, methanol, or ethanol by the reduction of CO₂ in water. The latter can be termed “artificial photosynthesis,” since biological photosynthesis uses the same reactants of CO₂ and H₂O to form biomass and O₂. However, the term “artificial photosynthesis” is also applied more generally to all fuels and chemical products produced via solar photochemistry. The photoactive molecules and materials used to create and separate electrons and holes and to drive the appropriate redox chemistry are semiconductors (inorganic or organic) in photoelectrochemistry, molecular structures in photochemistry, and biological structures (e.g., *in vivo* water-splitting blue-green algae or *in vitro* reaction centers) in photobiology.

The best reported conversion efficiency (rate of H₂ free energy output divided by the input solar power) for the photolytic splitting of water by semiconductor structures is about 12%. This efficiency was achieved using a monolithic tandem cell structure that consisted of two series-connected p-n junctions of GaAs and GaInP₂ with noble metal catalysts deposited on the anodic (oxygen evolving) and cathodic (hydrogen evolving) sides of the layered structure. However, the cost of this cell is very high, and the use of such high-efficiency tandem cells is usually reserved for space applications. Photobiological production of hydrogen by photosynthetic blue-green algae has recently been achieved without the usual poisoning of the algae by the evolved oxygen. However the conversion efficiency is very low (< 1%). Systems in between these limits, in terms of both cost and efficiency, have also been developed and include the photoelectrolysis of aqueous HBr using Si microspheres and the photoelectrolysis of aqueous HI using pure semiconductor crystals. Combination approaches are also possible in which non-biological chromophores are used to drive photosynthetic processes in cells and, conversely, in which photosynthetic reaction centers are modified to produce different fuels than are normally produced by the natural biological system.

Underlying all of these approaches are inexpensive photoconversion systems and effective, robust fuel-forming catalysts. The reactions of interest are multi-electron transfer processes that are difficult to perform near their thermodynamic potential using known inexpensive catalysts. Important targets include the direct photochemical splitting of water into H₂ and O₂, catalysts that individually reduce water to hydrogen and oxidize water to oxygen and that could be used either in an integrated fashion with photoelectrochemical devices or in a modular fashion with PV systems, and catalysts that effect the reduction of CO₂ to organic fuels (e.g., methanol or methane) or that utilize H₂ with CO₂ to form hydrocarbon fuels.

New Scientific Opportunities

Biological systems offer proof of concept that such catalysis is possible, because enzymes such as hydrogenase, nitrogenase, and the oxygen-evolving components of photosystem II drive these fuel-forming reactions with extremely high energy efficiency. At present there is little understanding of how to remove such catalysts from the biological system and maintain their function or how to design biological catalysts for such reactions that are inexpensive and robust under expected operating timescales and environmental conditions. There is a critical need to develop catalysts, likely transition-metal based, that can enable this fuel-forming function, whether in direct solar conversion systems or as a module in conjunction with solar-to-electric systems, and that as a system enable the production of fuel from the solar energy resource.

Relevance and Potential Impact

The same considerations for inexpensive conversion of solar energy apply to systems that would enable inexpensive storage and fuel production from solar energy. All the possible strategies for high-efficiency, low-cost, high-stability and long-lifetime solar photoconversion systems must be examined and compared to find the optimum system(s) to achieve the important goals described above for producing stored chemical free energy in fuels or electricity from renewable resources. This is particularly vital since photoconversion is a direct solar conversion process that utilizes the largest available renewable energy resource and has the potential to operate with ultrahigh conversion efficiencies and with very low-cost materials in an integrated system that provides the solar energy conversion and storage functions while producing useful fuel from a renewable energy resource.

Estimated Time Scale

10-20 Years

ADVANCED MATERIALS FOR RENEWABLE ENERGY APPLICATIONS

EXECUTIVE SUMMARY

Photovoltaic conversion is one of the leading contenders for renewable energy sources. The basic physical principles of photoconversion are now well understood, leaving system design and materials development as the primary challenges for widespread implementation. Solar cells made from polycrystalline (including amorphous silicon, a-Si) semiconductors on low-cost substrates are a promising direction requiring significant materials advances. Hybrid solar cells combining a porous wide bandgap semiconductor with a light-sensitive dye offer high potential for low-cost unconventional photovoltaic conversion. Opportunities and prospects associated with hybrid conversion materials are very promising and create many attractive materials research directions. In the longer term, nanostructured materials offer qualitatively new opportunities and challenges for solar conversion, exploiting quantum dots, carbon nanotubes and nanofibers, and organic semiconductors. Early successes demonstrate significant impact of nanoscale materials on photoconversion and promise dramatic advances in material design and performance.

Summary of Research Direction

The most likely scenario for renewable energy utilization generally envisions a mix of technologies, with photovoltaics (PV) being the leading contributor. The factors that are most detrimental to widespread PV applications are cost and effective storage of the electrical energy produced. The storage problem is such a severe limitation that any discussion of materials for PV conversion for the future should include consideration of materials problems relating to the storage device (e.g., batteries) itself. Revolutionary progress in photovoltaic conversion of energy depends on developing materials that will work effectively, reliably, and are inexpensive to implement.

Single crystal conventional cells. Consider first high efficiency single-crystal silicon cells. Efficiencies have progressed to a remarkable point in the last 10-15 years, but at an enormous increase in the cost and complexity of the cells. The materials problems associated with Si itself have largely been overcome because of its widespread use in the semiconductor industry. Recent gains in efficiency have been made by improved fabrication techniques for antireflection coatings, texturization of the surface for light trapping, buried contacts to increase the active area, etc. If one considers other semiconductors such as GaAs, the materials situation is less well developed, but still the research has been at a respectable level. Multi-junction cells, even for concentrator applications, are very complex and the materials issues even more demanding. Again, these avenues have been thoroughly explored and it seems that a breakthrough of the magnitude needed is not to be found in this area. The driver is not efficiency, but cost.

Thin-film cells on low-cost substrates. The driving force for the development of this approach to PV is again cost. The high-efficiency cells mentioned above all utilize the material itself to support the active part of the cell. Even in Si with its indirect bandgap, very little of the material is utilized for the actual PV conversion. Consequently, thin films deposited on low-cost substrates would seem to offer a path to drastic reductions in cost. Let us consider three such paths that have been extensively explored.

At one time, a-Si solar cells were considered the hope of the photovoltaic industry for large-area applications, but their potential has not been realized and now almost universal pessimism about them prevails. For one thing, degradation due to Staebler-Wronski effect has not been satisfactorily overcome. Efficiencies remain

comparatively low. To increase the efficiencies, research on multi-junction a-Si cells has been pursued, but the fabrication of such cells is costly and the efficiency/cost equation was never that favorable for them. Also, there is the question of the substrates, usually glass or very thin stainless steel, which can become prohibitively expensive in the quantities and quality needed. Materials research for a-Si has been both intensive and extensive and it is difficult to identify new areas that might lead to a breakthrough.

Another somewhat similar approach uses polycrystalline Si on low-cost substrates. The problems here arise primarily from grain boundary effects in the semiconductors and interdiffusion from the highly impure inexpensive substrates. To minimize grain-boundary effects, the grains must be fairly large, which puts severe restrictions on deposition processes. High temperatures (near the melting point of Si) are required for the film deposition itself or else a subsequent recrystallization step must be introduced. In either case, the demands on the low-cost substrate materials at these high temperatures are extremely severe. Although progress with this approach has been slow to date, it is possible that a concerted effort in the materials area could yield truly worthwhile gains.

Yet another approach in this category that has been extensively studied utilizes thin films of small-grained, direct bandgap materials such as CdTe and CuInSe₂ on low-cost substrates. Here, the deposition temperature may be quite reasonable and not a problem, although the deposition process itself requires close control. It remains an area where further research could be fruitful. The grain-boundary effects in these materials, often quite subtle, are still not well understood nor readily controlled. Consequently, reproducible fabrication is a problem.

Dye-sensitized mesoporous solar cells. A recent, very encouraging development is the success some groups have had with the so-called Grätzel cell. In this approach, a porous, fairly wide band gap semiconductor such as TiO₂ is impregnated with a light-sensitive dye (usually a transition metal complex whose molecular structure is specifically designed to have the required properties). The dye absorbs the photons and the excited electrons are injected into the conduction band of the TiO₂. Electron-hole separation occurs so rapidly at the TiO₂/dye interface that recombination is practically eliminated. Because the internal surface of the film is much higher than its projected geometric surface, there is a large interfacial area between the dye and the semiconductor. Due to the small size of the particles/pores, the film does not scatter visible light. Also, visible light is not absorbed by the oxide if the bandgap is large enough.

Solar cells from nanophase materials. Since the pores in the porous materials of the Grätzel-type cell may be very small, the conceptual progression to nanophase materials is a natural one. While it is too early to predict what the impact of nanoscience engineering and technology on PV conversion may have, it is difficult to believe that it will be of no consequence. The capability to tailor both optical and electrical properties of arrays of quantum dots has already been demonstrated. The outstanding electrical, thermal, and mechanical properties of carbon nanotubes and nanofibers are widely appreciated, even though severe obstacles to their applications in large-scale systems remain formidable. The flexible thin-film features of both nanophase and organic semiconductors are important for applications, leading perhaps to photovoltaic “cloth” and “plastic wrap”. The already well-established self-organizing capabilities of some systems, such as block copolymers and nanoporous oxide templates, could be important for Grätzel cell type applications.

New Scientific Opportunities

Thin-film cells on low-cost substrates. In the area of low-cost substrates, concerted efforts in materials areas could yield truly worthwhile gains. Efforts should be aimed at understanding and controlling grain boundaries better and the development of substrates that retain their low cost while remaining practically inert to the thin-film deposition process itself. In particular, reproducible fabrication techniques are desperately needed. Intensive materials research in this area of grain-boundary effects might lead to steady progress, if not to a breakthrough.

Dye-sensitized mesoporous solar cells. While the efficiencies that have been obtained so far are relatively modest (~10%), the approach is quite different from the conventional ones described above and warrants much further study. Unlike conventional cells, the light absorption process and the electron-hole charge separation are differentiated. A multitude of crucial questions about the most effective materials and materials combinations (semiconductors and dyes) remain to be explored. Since the dyes are frequently organic materials, the oft-discussed marriage of organic and inorganic materials, primarily semiconductors, is a fundamental aspect of the approach. It perhaps should also be pointed out that porous materials of a somewhat similar type are expected to have important applications for catalysis and a variety of other technologies. Thus, a wider spectrum of scientific expertise might be brought to bear on the problems. This is an exciting area for fundamental materials research with practical applications.

Solar cells from nanophase materials. The possibilities for nanophase materials are too numerous to be discussed here, but their potential importance is undeniable.

Relevance and Potential Impact

Within DOE, successful research on new materials for renewable energy is particularly relevant to the Energy Efficiency and Renewable Energy Program on Solar Energy Technology. Since nanomaterials will potentially play a prominent role in new approaches to photovoltaic materials, the research is directly related to the National Nanoscale Science, Engineering, and Technology initiative that crosses many federal agencies.

Estimated Time Scale

Materials research on conventional single-crystal solar cells is well developed and evolutionary progress is expected to continue. The materials issues governing the performance and cost of polycrystalline, thin-film solar cells and a-Si are much less well understood and are likely to see significant breakthroughs enabling discontinuous progress in the next five years or more. Progress on dye-sensitized mesoporous cells requires path-breaking research on photoconversion and charge collection in hybrid materials, a promising and fertile opportunity for creating qualitatively new materials with tailored properties over the next ten or more years. Nanophase materials for photovoltaics offer the broadest horizon and the highest potential for spectacular progress. Understanding and controlling the behavior of single- and multiphase photoconversion materials at the nanoscale can make revolutionary progress in the cost and performance of solar cells. This area is now in its infancy and will be fruitful over the next two decades or more.

Fusion Energy

**Multiscale Modeling of Microstructural Stability
of Irradiated Materials**

Deformation and Fracture Modeling

Plasma-Surface Interactions

Thermofluids and “Smart Liquids”

Plasma Aerodynamics

MULTISCALE MODELING OF MICROSTRUCTURAL STABILITY OF IRRADIATED MATERIALS

EXECUTIVE SUMMARY

Fundamental research is needed to identify the key physical processes that will enable materials to maintain microstructural stability during prolonged fusion neutron irradiation. By utilizing physically rigorous bridging of the gaps between different spatial and temporal modeling regimes (nanoscale to continuum), a comprehensive predictive capability for modeling the stability of prospective advanced nanoscale materials can be attained. Several longstanding, unresolved materials science issues could be answered by this research program (e.g., “one-interstitial” versus “two-interstitial” model for point defect migration). The successful development of fusion energy will require materials that are capable of withstanding exposure to intense radiation fields over a broad range of temperatures. A sound physics-based understanding of the stability of materials in the anticipated fusion environment is key for establishing the viability of fusion as a future energy source. This fundamental information is also of importance for advanced Generation-IV fission reactor materials.

Summary of Research Direction

Materials are key to achieving attractive fusion energy. Opportunities in the area of multiscale materials modeling for a comprehensive predictive capability of the response of fusion materials are extensive. They range from basic theoretical developments of fundamental processes at the atomic, mesoscopic and continuum scales to highly complex simulations of surface and bulk phenomena. Surface processes include sputtering and other erosion mechanisms, implantation, re-deposition and co-deposition of tritium, near surface damage and microstructure evolution, enhanced atomic transport (diffusion, trapping/detrapping and desorption), and surface roughening and restructuring. Bulk processes include crystal lattice displacement damage, creation of atomic and clustered defects, microstructure evolution (e.g., voids, bubbles, dislocations and new phases), dimensional instabilities (e.g., swelling and creep), shear bands and localized plasticity, and a host of embrittlement phenomena at both low and high temperatures. The recommended approach is to utilize multiscale materials modeling, covering atomistic simulations (e.g., ab initio quantum methods, molecular dynamics, and Monte Carlo), mesoscopic simulations (e.g., dislocation dynamics and statistical mechanics), and continuum simulations (e.g., rate theory and the Finite Element methods). A critically important aspect of the multiscale materials modeling is to use physically rigorous bridging of the gaps between the various spatial and temporal modeling regimes. Specific recommended thrust areas associated with this multiscale modeling paradigm include the following:

- Development of improved interatomic potentials, including directionality effects, magnetic effects (very important for ferritic steels), alloying effects. Since interatomic potentials are the fundamental building blocks used for many higher-scale materials models, it is crucial that these descriptions of atomic interactions be physically meaningful. It is well known that many of the state-of-the-art interatomic potentials currently available do not accurately describe many fundamental material properties, and therefore further work using atomistic and quantum chemical techniques is needed to achieve improved, more realistic descriptions of the interatomic interactions.
- Numerous recent molecular dynamics (MD) simulations (using interatomic potentials of dubious quantitative accuracy) have predicted the possibility of long-range one-dimensional transport of

matter via self-interstitial crowdion bundles. This mechanism has enormous potential consequences on the interpretation of existing experimental data (due to the different reaction kinetics for 1-D versus 3-D transport), and reopens the highly controversial condensed-matter physics debate (dating back to the 1960s and never fully resolved) regarding the “one-interstitial” versus “two-interstitial” model for point defect transport. The prospect of 1-D migration of defect clusters would also have an impact on non-nuclear fields, for example, semiconductor processing by ion beam implantation methods (providing either an obstacle or an opportunity for creating unique nanoscale structures via ion implantation).

- Development of physically rigorous multiscale microstructural evolution models based on molecular dynamics, kinetic Monte Carlo and kinetic rate theory techniques. The predictions from these multiscale materials models would be experimentally validated by comparison with specific well-controlled experiments performed on model metallic and ceramic material systems. An overarching question associated with this activity is whether nanoscale structures can be designed with extremely high resistance to radiation damage and transmutant helium degradation.
- Phase stability under irradiation, with particular emphasis on the following three aspects: (1) development of improved physics-based models of radiation-induced or -enhanced solute segregation to interfaces (grain boundaries, etc.) due to inverse Kirkendall, solute drag, and other mechanisms; (2) evaluation of the effect of solute segregation on corrosion resistance; and (3) displacement cascade dissolution of second-phase particles (most of the available models date from the 1970s and do not correctly predict the experimentally observed behavior). Improved models are needed to describe both solute segregation processes and precipitate/solute cluster ballistic dissolution processes. Specific materials systems of interest for fusion applications include the stability of (Y, Ti, O) clusters in nanocomposited ferritic steels and Ti(C,O,N) precipitates in V alloys.
- Transport and clustering of helium. Helium produced by nuclear transmutation events may ultimately determine the operating lifetime and maximum use temperature of materials in fusion systems. Grain-boundary embrittlement due to accumulation of helium bubbles is a well-known phenomenon that limits the maximum operating temperature of helium-containing materials, but recent experimental research suggests that special types of grain boundaries may exhibit significantly different response to helium accumulation. A fundamental understanding of the role of different types of grain boundaries on helium transport within the grain boundary is lacking. If this effect could be properly understood, it might eventually lead to developing materials with specifically designed grain boundaries in order to attain significantly higher resistance to helium grain boundary embrittlement.

New Scientific Opportunities

By utilizing physically rigorous bridging of the gaps between different spatial and temporal modeling regimes (nanoscale to continuum), a comprehensive predictive capability for modeling the stability of prospective advanced nanoscale materials can be attained. This research could answer several longstanding unresolved materials science issues (e.g., “one-interstitial” versus “two-interstitial” model for point defect migration).

Relevance and Potential Impact

The successful development of fusion energy will require materials that are capable of withstanding exposure to intense radiation fields over a broad range of temperatures. A sound physics-based understanding of the stability of materials in the anticipated fusion environment is key for establishing the viability of fusion as a future energy source. This fundamental information is also of importance for advanced Generation-IV fission reactor materials.

Estimated Time Scale

- ~10 years: development of improved interatomic potentials (including directionality effects, magnetic effects, alloying effects)
- ~10 years: multiscale microstructural evolution and nanoscale solute segregation models of irradiated materials based on Molecular Dynamics and kinetic Monte Carlo techniques
- ~10 years: development of improved physics-based models of radiation-induced or -enhanced solute segregation to interfaces (grain boundaries, etc.) and their resultant effect on corrosion resistance

DEFORMATION AND FRACTURE MODELING

EXECUTIVE SUMMARY

A fusion energy system requires a high level of material performance to function safely and economically. In a fusion energy system, structural materials must perform at damage levels and with gaseous and solid transmutants well beyond those of other nuclear systems. Multiscale modeling of material deformation and fracture is of tremendous need for fusion energy systems, because this can accelerate the design and development of materials to meet these demands while comprehensive models could also aid in the design process as well. New opportunities exist to understand and predict the effects of radiation on deformation and fracture. Multiscale modeling involving atomistic simulations (e.g., ab initio quantum methods, molecular dynamics, and Monte Carlo), mesoscopic simulations (e.g., dislocation dynamics and statistical mechanics), and continuum simulations (e.g., rate theory and the finite element methods), coupled with greatly expanded computational capabilities, allow us to understand phenomena and predict behavior beyond that which has been possible with experimental approaches.

Summary of Research Direction

New multi-scale modeling opportunities that cover the atomistic to continuum scales exist today and can provide new fundamental understanding of some complex problems that have been studied for a number of years. This includes understanding of radiation effects problems that have been studied for a number of years along with application to understanding and predicting the behavior of new materials. The introduction of new materials, such as nanoscale reinforced materials and radiation resistant composite materials, into fusion energy systems can occur in a shorter time frame with the fundamental understanding that is possible with new modeling. Also, a better understanding of radiation phenomena will also allow tailoring of conventional materials to gain improved performance. Some examples covering both new materials and a description of some well-known problems are given below.

- Newly developed ceramic matrix composites present new opportunities for radiation environments and challenges to model their deformation and fracture behavior. Multiscale modeling must incorporate details from the atomistics of the fiber/matrix interface (e.g., effect of gaseous transmutants, thermal transport, and interfacial fracture strength) to a model for the bulk deformation based on localized microcracking.
- This topic was highlighted at a recent NE/BES workshop on Higher Temperature Reactor Materials (ANL-02/12, June 2002). It is critically important for Generation-III+ and -IV fission reactors and future fusion systems to develop materials that do not suffer unacceptable degradation in ductility and fracture toughness during low-temperature neutron irradiation. The international fusion materials community is actively investigating many of the underlying mechanisms responsible for the mechanical property degradation. Teaming with BES researchers would lead to acceleration in the understanding of the mechanisms. Key issues include: (1) dislocation interactions with SFTs, (2) conditions for or limiting cross-slip of irradiated materials, and (3) physics of channel development and effects on fracture
- Radiation embrittlement can now be understood at the atomistic level and in fact semi-empirical modeling has been successful in predicting shifts in the fracture transition from ductile to brittle

behavior. However, improved interatomic potentials and multi-scale models incorporating dislocation dynamics have the capability to reveal new insights into our understanding of radiation embrittlement. This knowledge at the atomistic level could provide the opportunity to design new radiation resistant materials.

- Radiation embrittlement and fracture deal with the initiation of flaws that are critical in size in terms of conventional fracture mechanics. Subcritical sized cracks initiate and grow with time to become critical sized flaws that induce fracture. The initiation and propagation of subcritical sized flaws often involve interactions between external and internal nano- and microchemistry, nano- and microstructure and loading conditions at the tip of a crack. There are opportunities to use ab initio modeling of local chemistry, molecular dynamics modeling of crack-tip deformation, mesoscale modeling of plastic zone scale processes and continuum modeling of far-field effects to provide new insight and understanding to this field. A key challenge involves merging chemistry, physics and mechanics modeling tools.
- High-temperature deformation mechanisms, such as irradiation creep, have been the subject of numerous fundamental research projects over the past 40 years or so, but one of the important new twists is the possibility that new nanoscale materials may behave differently from conventional materials (recent experimental results on nanoscale oxide-dispersion-strengthened ferritic steel suggests this may be the case). If nanoscale structures can be tailored to provide superior creep strength, this could usher in a whole new class of high-performance materials for a broad range of applications. Another new twist is the high-temperature deformation, creep and irradiation creep of ceramic composites. These materials deform by local microcracking and link-up to produce macroscopic strain. Comprehensive models describing irradiation effects on high-temperature deformation and fracture are needed.

New Scientific Opportunities

The current understanding of radiation effects on deformation and fracture of new materials is inadequate. New multi-scale modeling capability has the potential to make breakthroughs in understanding and designing these new materials.

Relevance and Potential Impact

A fusion energy system requires a high level of material performance to function safely and economically. In a fusion energy system, structural materials must perform at damage levels and with gaseous and solid transmutants well beyond those of other nuclear systems. Multiscale modeling of material deformation and fracture is of tremendous need for fusion energy systems because this can accelerate the design and development of materials to meet these demands. Comprehensive models could also aid in the design process as well.

Estimated Time Scale

Considerable phenomenological understanding of radiation effects on deformation and fracture has been obtained over an extended period. Modeling developments have also been occurring over a shorter time period than the experimental work but still over a relatively long period of time. These time periods were needed because of the complexity of the problem. Opportunities for utilizing multi-scale modeling to

understand and predict these complex problems exist today but will also require an extended period because: (1) models must address complex systems and (2) experimental verification of the models will require an extended period of time. Given the current schedule to produce a fusion demonstration plant and the time frame for bringing new materials to commercial production, these results are needed in the next 10 years.

PLASMA-SURFACE INTERACTIONS

EXECUTIVE SUMMARY

One of the most important issues concerning the basic feasibility of fusion as an energy source, and a major issue for present-day high-temperature plasma confinement experiments, is the interaction of intense heat and particle fluxes with plasma-facing components. These interactions need to be understood in terms of the basic phenomena so that they can be controlled. Potential impacts include contamination of the plasma and short lifetimes of the components.

Another related issue is developing high-power targets for future accelerators and particle colliders for nuclear and high-energy physics as well as for space applications. Understanding basic mechanisms of material destruction and lifetime enables the design and development of materials that meet these harsh environments. This effort will increase the basic understanding of critical issues related to plasma-surface interactions including photon radiation transport, “potential” sputtering, and material erosion under intense power loadings. Developing multi-scale and integrated models of these issues using powerful computational capabilities will significantly increase our basic knowledge to best optimize and enhance plasma and material performance.

Summary of Research Direction

One important area that determines many of the plasma-surface interaction effects is photon radiation and transport in both optically thin and optically thick plasmas with intense line populations. Developing 3D direct photon transport computer models (Monte Carlo, ray tracing, etc.) in a highly charged, hot and dense plasma is quite important in various basic research areas. This is an extremely important effect, since it will define/control plasma time evolution and the degree/intensity of plasma-material interactions of nearby components.

Another important topic is a recently discovered physical phenomenon that is not well understood called “potential sputtering”. This occurs during the interactions of highly charged ions with target materials. The sputtering coefficient is several orders of magnitude higher than the values for well-known physical sputtering (100-1000 times). An important related area is basic understanding of details of interatomic potentials. Developing phenomenological models and 3D molecular dynamics methods to understand this effect is, therefore, highly desired. This has many potential benefits, such as preventing “explosive” erosion of materials or the use of these methods for highly effective etching of materials.

Understanding fundamental models of material erosion and destruction under intense power applications is another vital topic. Material destruction and lifetime issues take many forms including fragmentation, splashing, brittle destruction, spallation, etc. Most of these issues require detailed understanding of the microstructure evolution dynamics during the intense-power deposition phase. Up to now there is no comprehensive understanding of all of these effects. These issues are of significant concern in many basic research science [e.g., beam/plasma-on-target effects for high-energy physics (muon collider, neutrino project)], nuclear physics [high-power accelerator, Spallation Neutron Source (target concerns)], medical applications (high-power electric arc effects and injuries), and plasma interactions with electrodes in plasma guns, Z-pinch, dense plasma focus, and others.

New Scientific Opportunities

Development of a deeper understanding and models for key plasma-surface interactions involving intense particle and heat loads.

Relevance and Potential Impact

One of the most important issues concerning the basic feasibility of fusion as an energy source, and a major issue for present-day high-temperature plasma confinement experiments, is the interaction of intense heat and particle fluxes with plasma-facing components. These interactions need to be understood in terms of the basic phenomena so they can be controlled. Potential impacts include contamination of the plasma and short lifetimes of the components.

Another related issue is developing high-power targets for future accelerators and particle colliders for nuclear and high-energy physics as well as for space applications. Understanding basic mechanisms of material destruction and lifetime enables the design and development of materials that meet these harsh environments.

Estimated Time Scale

The research activities described here have typically a 10-year period.

THERMOFLUIDS AND “SMART LIQUIDS”

EXECUTIVE SUMMARY

The proposed research is to develop a fundamental understanding of, and capability to control, flowing electrically-conducting fluids in complex environments that include electromagnetic fields. Magnetohydrodynamic (MHD) forces can affect liquid motion from the largest, integral scales down to the finest scales of turbulence. These fundamental changes in the liquid motion have an impact on practical considerations, like how much energy it takes to force fluids to flow through pipes or what happens to hot interfaces when subjected to intense heating conditions.

MHD phenomena also provide one means of controlling the liquid flow to mitigate undesired consequences and even improve the capability of a fluid flow to perform some function. Clever ideas that modify local magnetic field or supply externally injected electric currents may be utilized to accelerate liquids in desired directions. This electromagnetic control may be necessary for the use of liquids as virtual first walls of magnetic and inertial confinement fusion reactors, where they would act as continuously self-healing surfaces in contact with the burning plasma, one which would be immune to radiation damage effects. Other ideas to modify the fluid properties themselves through chemical systems engineering and micro and nano technologies could potentially work hand-in-hand with electromagnetic effects to maximize potential for a given engineering application. Ultimately, fluid properties can be tailored so that such “smart liquids” can be shaped and steered, as well as mixed and separated in such novel fashions only now being conceived.

Summary of Research Direction

From the fusion perspective, the establishment of liquid walls or liquid surface divertors (for MFE and IFE) that allow high-heat-flux handling, high reliability, long lifetime and high efficiency heat extraction would be extremely significant. The behavior of such unrestrained flows in complex, temporally and spatially varying magnetic and electric fields poses a significant challenge in terms of numerical and experimental simulation. Magnetohydrodynamic forces can affect the liquid motion from the largest integral scales all the way down to the finest scales of turbulence. The particle- and heat-removal capabilities of such flows will depend heavily on the flow conditions, so that accurate simulations are necessary for the determination of feasibility and performance. Even for more conventional closed-channel cooling systems, similar motivation for better understanding of interactive, multi-scale flow processes and heat transfer exist. The ultimate idea is something like the creation of “smart liquids” via a number of engineering science disciplines. Specific suggestions that might be of interest to BES include the following:

- Numerical simulation of the effect of magnetohydrodynamic forces on turbulence in incompressible and stiffly compressible liquid conductor flows and their related transport of heat and mass, especially near solid and free interfaces. Studies can include: (1) evolution of 3D turbulence entering strong magnetic fields regions to 2D-like turbulence to complete turbulence suppression, (2) turbulence generated from shear flows completely “grown” inside a strong magnetic field, (3) instability and collapse of boundary layers and shear layers, and (4) compressible effects coming from rapid heating and incident surface shocks.

- Control of liquid-metal flow motion and velocity profiles via applied magnetic and electric fields and currents. The ability to control the flow of free-surface liquid-metal walls is a similar challenge to the magnetic control of fusion plasma itself. Simulation of the motion of the liquid wall, including interaction with complex geometry, electrically conducting structures, and electromagnetic coupling to the plasma will be an important part of establishing the feasibility of the liquid wall idea.
- Modification and control of fluid properties and behavior via complex chemical doping and micro-additives. Taking advantage of the revolution in MEMS and nano-technology and new simulation capabilities for chemical/material systems, concepts and basic proof-of-principle simulations and experiments should be developed to apply these ideas to the control of the micro-processes in the liquid flows to give benefits like reduced-surface evaporation; improved surface gettering of hydrogen, helium and impurities; reduced wall corrosion; and many others.

New Scientific Opportunities

Several avenues for improvement in computation methods for complex physical problems are mandated by this work.

- 3-D direct numerical simulation (DNS) and large eddy simulation (LES) and other methods of incompressible, turbulent, free-surface fluid flow in strong electromagnetic fields and complex geometries. Improvement of free-surface tracking techniques like Level-Sets and Front Tracking will be required, as well as complex unstructured finite-volume and finite-element grids.
- Stiffly compressible liquid modeling, with intense sources of heat and particles that allow for phase change, cavitation and fracture of initially condensed liquid flows. Free-surface tracking techniques like Phase Field and accurate equations of state will be required.
- Near-surface molecular dynamics and similar techniques to simulate changes in surface properties from dopants and nano-additives as well as kinetic interaction with energetic particles.

Application and expansion of these numerical modeling techniques to gain better efficiency and fidelity in simulating these complex multi-scale physical systems, as well as data-visualization techniques required to interpret the voluminous data.

Relevance and Potential Impact

Fusion energy seeks to contain star-like conditions within physical barriers. The environment includes elevated temperatures, radiation and kinetic debris. To solve the resulting materials problems, increasing attention is being given to liquid walls in both magnetic and inertial fusion. Liquids can be pumped through the harsh reactor environment and out to a benign area where liquid refurbishment can be performed. “Smart liquids” may enable unique solutions to direct flow, especially free-surface flow in complex, fusion reactor geometries, and control heat-transfer and particle-pumping effects that depend heavily on the small-scale near-surface turbulent motion.

The impact of smart liquid development would hardly be confined to the fusion reactor application only. The control of free-surface flows by electromagnetic and other means has a myriad of potential applications in industry including fuel injectors and other combustion processes, water jet cutting, ink jet printers,

continuous casting, flood/jet soldering, hull design, ocean/river hydraulic engineering, crystal growth and many others.

Estimated Time Scale

The feasibility of employing liquid wall concepts in fusion power systems should be established in the next 10-20 years. The in-depth, scientific understanding of the thermofluid science involved in such concepts should be established in the next 10 years.

PLASMA AERODYNAMICS

EXECUTIVE SUMMARY

Efficient access to space, hypersonic transport, and the development of high-performance re-entry vehicles are areas of national importance. Vehicles that operate in these regimes suffer from extremely high heat loading and must contend with very complex flow physics, including laminar-to-turbulent transition, shock wave boundary layer interactions, nonequilibrium gas dynamics, and supersonic combustion. For air-breathing hypersonic vehicles, the inlet geometry must be mechanically modified for each flight Mach number to avoid unacceptable performance and catastrophic engine stall. It has recently become apparent that the use of weakly ionized plasmas may revolutionize the capabilities of these vehicles. Weakly ionized plasmas can be used to locally deposit energy into the air to control shock location, produce virtual vehicle geometries, control transition to turbulence, reduce drag, avert engine stall, and accomplish other objectives not currently possible with mechanical devices. In addition, weakly ionized plasmas are electrically conducting, and, therefore, provide the opportunity of incorporating magnetohydrodynamics into the vehicle design for control, power extraction, thrust augmentation, and vehicle steering. The potential application of these concepts involves a detailed understanding of plasma formation properties, including nonequilibrium molecular phenomena, plasma contraction and filamentation, electron beam interactions, microwave coupling; and other approaches to achieve both high-efficiency energy deposition and high-efficiency generation of conductivity. Modeling of aerodynamic processes must include full electromagnetically coupled, dynamic three-dimensional flow-field calculations, including nonequilibrium and turbulence.

Summary of Research Direction

The area of plasma aerodynamics is just beginning to be explored. There are numerous fundamental issues that need to be understood.

- Because the plasmas are so expensive in power to establish and sustain, one of the critical areas to understand is the time scale of the phenomena. Moving from continuous to pulsed plasmas may reduce the overall power requirement and improve the performance of the process. It is important to know how long various effects last after the plasma is turned off and whether pulsing is preferable to continuous operation. It may also be possible to achieve the desired plasma effects by using nonuniform plasmas that consist of streamers or multiple simultaneous or sequentially formed localized plasmas. This may further reduce the power requirement.
- In many of the plasma aerodynamic applications, the presence of instabilities may become a serious limitation. Filamentation will cause a glow discharge to collapse and generally happens when the pressure rises and where large electric field gradients are present. This may limit the operation of MHD power extraction or low observability plasmas. On the other hand, filamentation permits the delivery of large amounts of heat to localized regions, so it may be preferable in some circumstances. The high velocity of the flow, high magnetic field strength, and the coupling of the plasma to the flow may lead to unexpected instabilities.
- Mechanisms for the efficient creation of air plasmas also need to be understood. These may be very different depending on whether the plasma is needed for conductivity or for heat addition.

- Perhaps the most difficult issue is the establishment of scalability relations. Almost no experiments can be done on full-scale vehicles, so the community will be relying on sub-scale experiments. The very different nature of plasmas as a function of air pressure, temperature, electric and magnetic field strength, fluid motion, and molecular species make sub-scale experiments very difficult to extrapolate. Numerical simulations may help guide development of flight tests to generate scalability data.

New Scientific Opportunities

A plasma aerodynamics program will establish models for treating the interaction of plasma and electromagnetic forces with three-dimensional flow fields and aerodynamic shapes. Since, in general, aerodynamic plasmas are expensive to create, it is important to understand the impacts that they may have on vehicle control, heat-load mitigation, and performance enhancement. For example, the ability to control the inlet shock structure may remove the need for hydraulically-driven inlet flaps and deformable duct walls. Since a large fraction of the aircraft weight is associated with these mechanical devices, the cost penalty of the plasma formation mechanisms may be small by comparison. Plasmas and MHD processes provide the capability of achieving new methods for controlling air flow and may enhance the capabilities of the vehicle well beyond those that can be achieved with mechanical systems. For example, modeling suggests that off-body plasmas can be used to suppress far-field shock coalescence and, therefore, minimize sonic boom. If this is true, it may open up supersonic flight to commercial air transport. New plasma technologies combined with new multifunctional lightweight materials may provide highly capable re-entry vehicle geometries with low-heat loading or wide cross-path landing capability for emergency return of astronauts. The scientific opportunities focus on understanding the effects that plasmas can have on aerodynamic interactions with vehicles for control, power extraction, heat-load mitigation, and performance enhancement.

Relevance and Potential Impact

Weakly ionized air plasmas have a high potential for impact on advanced aerodynamics. Specifically, plasmas and MHD processes may be capable of mitigating peak thermal loads, extracting high levels of power, reducing drag, reducing observability, reducing sonic boom, and suppressing noise. Plasmas may be employed to facilitate stability and control by optimizing inlet shock position, controlling turbulence by initiating or suppressing transition, and steering the vehicle with localized heat addition. Internal aerodynamics may be affected by virtual shaping of the internal ducting through plasma heating, elimination of shock reflections by localized surface plasmas, enhanced mixing, and control of ignition and enhancement of combustion rates.

Estimated Time Scale

Research activities have a 5-10 year period.

Distributed Energy, Fuel Cells, and Hydrogen

Advanced Hydrogen Synthesis

**High-Capacity Hydrogen Storage for Distributed
Energy of the Future**

Novel Membrane Assemblies

Designed Interfaces

ADVANCED HYDROGEN SYNTHESIS

EXECUTIVE SUMMARY

Hydrogen has the potential to offer solutions to two major challenges in future growing energy use, the security of the energy supply and the preservation of the environmental quality. To realize this potential, our understanding of the principles of hydrogen usage, and their development and incorporation into novel technologies for massive hydrogen synthesis systems, needs to be accelerated.

Currently, about 9 million tons of hydrogen are produced per year in the U.S. alone, primarily from steam reforming of fossil fuels such as natural gas. While natural gas can continue to supply hydrogen for the near term, in the mid-to-long term (>20 years), other production technologies using sustainable feedstocks must be brought on line. Mid-to-long-term processes that hold promise to produce hydrogen domestically, without net CO₂, emissions include gasification of biomass or organic wastes, electrolysis of water using electricity from renewable resources (i.e., photovoltaic, wind, solar-thermal-electric, and geothermal) or nuclear power.

Fundamental advances in catalysis, membranes, and gas separation could enable more efficient, lower cost fossil hydrogen processes. Understanding the feasibility of carbon capture and sequestration is key for long-term use of fossil hydrogen with near-zero emissions (i.e., geoscience and flows in porous media). Leap-frog technologies for the longer-term include solar photolytic methods and thermochemical water-splitting driven by nuclear or solar heat.

The direct and effective coupling of light harvesting to catalytic processes that produce hydrogen is a grand challenge. This builds on the BES research programs in photochemistry and catalysis. However, fundamental studies of catalysis need to be expanded to include electrocatalysis. Corrosion and materials selection are significant issues for semiconductor photolytic processes and in high-temperature thermochemical water-splitting systems.

Thermochemical water-splitting uses high-temperature heat (typically ~500 to 900°C) to drive chemical reactions to separate water into hydrogen and oxygen. One key to discovering, evaluating, and developing feasible and economic thermochemical water-splitting cycles is having a firm scientific basis for the chemical thermodynamic data, as well as for the models of the chemical reaction systems. The current thermal chemical cycles that are being considered for coupling to nuclear energy suffer from the need for materials that can withstand extreme corrosive environments at these elevated temperatures. Alternative cycles based on novel redox systems may be devised that operate at lower temperatures, thus reducing the daunting corrosion problems. For solar-driven systems, cycles that lend themselves to hot/cold (day/night) cycles can offer considerable potential if coupled with such reduced-temperature redox cycles.

Summary of Research Direction

Fossil Hydrogen Production. Today most commercially produced hydrogen is made at large scale from fossil fuels via steam reforming of natural gas or partial oxidation of heavier hydrocarbon feedstocks, such as residual oil or coal. Hydrogen is then used in chemical applications, including ammonia and methanol production and oil refining. Large-scale hydrogen production from fossil fuels for the hydrogen economy is

under consideration by oil companies such as Shell and British Petroleum (BP). A variety of small-scale fossil-based hydrogen production systems are under development for application to distributed hydrogen production (e.g., for use in fuel cells).

Light-Harvesting Systems Directly Coupled to Catalytic Processes to Generate Hydrogen. A photolytic process utilizes the fact that the entire visible spectrum of light has sufficient energy to split water into hydrogen and oxygen. Water is transparent and does not absorb this energy. The key then is to find an efficient light-harvesting system that can collect the solar energy and directly transmit towards a catalytic water-splitting reaction. Both photobiological and photochemical processes have shown the capability of using light energy to produce hydrogen and oxygen from water and sunlight. We propose fundamental studies of photoelectrochemical light-harvesting systems directly coupled to catalytic processes for hydrogen production.

Photoelectrochemical water-splitting, also known as photoelectrolysis, represents an advanced alternative to a photovoltaic (PV)/electrolysis system. The incident light, absorbed in a semiconductor electrode immersed in an aqueous solution, splits water directly. This is equivalent to combining a solar cell and an electrolyzer into a single monolithic device. In operation the semiconductor collects the light energy, and directs the energy to a catalyst on the surface of the semiconductor. Hydrogen is produced at the surface of an illuminated p-type semiconductor. Oxygen is produced at the surface of an illuminated n-type semiconductor. This occurs due to injection of electrons into the solution (for p-type) or because holes (e.g., electron vacancies) appear at the semiconductor/electrolyte interface (for n-type). The other component of the water-splitting reaction (oxygen or hydrogen, respectively) is generated in a separate compartment.

A one-step monolithic system of this configuration eliminates the need to generate electricity externally and subsequently feed it to an electrolyzer. This combination then reduces semiconductor processing, since surface contacts, interconnects and wiring are no longer necessary. Only the piping necessary for the transport of hydrogen to an external storage system or gas pipeline is required. An additional advantage of photoelectrochemical water-splitting is that H₂ and O₂ can be generated separately, and separation steps are not necessary. Another major advantage of a direct-conversion system is that the area used for electrolysis approximates that of the solar cell. Depending on the solar intensity and the type of semiconductor material, this translates to a current density of 10-30 mA/cm². At these current densities, the voltage required for electrolysis is much lower than standard electrolysis [in the range of 1.35 V (at 25°C)], and therefore the corresponding electrolysis efficiency is much higher [close to 90% (LHV)], resulting in an efficiency increase of up to 30% over a separated PV/electrolysis system, without the added cost of the electrolyzer. Finally, semiconductors can be very efficient light absorbers, resulting in a very high (>25%) theoretical solar-to-hydrogen conversion efficiency.

Thermochemical water-splitting cycles. Thermochemical water-splitting uses a set of thermally driven chemical reactions to separate water into hydrogen and oxygen. The process takes in only water and high-temperature heat and releases only hydrogen, oxygen and low-temperature heat. While high temperatures are needed (typically ~700 to 900°C), the heat can be provided by any source, including solar and nuclear energy. Advanced solar processes to produce hydrogen have significant potential, although basic research remains to be done.

New Scientific Opportunities

Fossil Hydrogen Production. Fossil hydrogen production methods, such as steam methane reforming, are well-established commercial processes, capable of providing hydrogen in large quantities. However, further research can optimize existing fossil hydrogen production approaches for use in future hydrogen energy systems. Fundamental advances in catalysis, membranes, and gas separation could enable more efficient, lower cost fossil hydrogen technologies. Processes that combine hydrogen generation and separation in a single reactor (for example, membrane reactors for methane steam reforming) could improve conversion efficiency and reduce emissions. Very pure (99.999%) hydrogen is needed for some applications, in particular proton exchange membrane fuel cells (PEMFCs), so that hydrogen purification technologies need further development.

Existing fossil-based hydrogen production processes release significant amounts of carbon dioxide. Near-zero emissions of greenhouse gases and air pollutants must then be a characteristic of future hydrogen production. Capture and sequestration of carbon during hydrogen production from fossil fuels are key technologies to enable long-term use of fossil-derived hydrogen. (This is particularly necessary for coal-derived hydrogen). Understanding the feasibility of carbon capture and sequestration is vital for long-term use of fossil hydrogen with near-zero emissions. This includes basic understanding of the geological processes that may be involved in carbon dioxide storage.

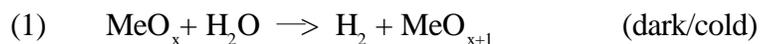
Light Harvesting Systems Directly Coupled to Catalytic Processes to Generate Hydrogen. The main issue with this approach is that the usual semiconducting materials that are stable in water and can do the water-splitting reaction do not absorb enough sunlight to be efficient, and the materials that absorb sunlight efficiently either corrode in aqueous solution or do not have the proper energetics to effect the water-splitting reaction. Research is needed that is directed at: (1) discovery of possible semiconductor materials that have appropriate light-absorption characteristics and are stable in aqueous solutions; (2) development of techniques for the preparation of catalytic coatings and their application to semiconductor surfaces; and (3) identification of environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.

An area of interest that is cross-fertilized with the solar industry is the study of photovoltaic multi-junction cell technology as applied to photoelectrochemical water splitting. Multi-junction cell technology connects photovoltaic layers (p-n junctions) with different semiconductor bandgaps in series, one behind the other in a single-cascade device. This arrangement provides the highest theoretical conversion efficiency of any photoconversion system (maximum of 66%). This approach may allow a material that would otherwise corrode in aqueous solution to be protected by another semiconducting material that is stable. The combination then provides a higher efficiency than each would offer alone.

Thermochemical water-splitting cycles. One key to discovering, evaluating and developing attractive thermochemical water-splitting cycles is having a firm scientific basis for the chemical thermodynamic data and models for the chemical reaction systems. Also critical is the need for materials that can withstand the corrosive environments and elevated temperatures projected for the current thermal chemical cycles that are being considered for coupling to nuclear energy. For example, in the S-I cycle, I_2 and SO_2 are added to water, creating H_2SO_4 and HI. These are separated and then decomposed by heating to release H_2 and O_2 and recycle the I_2 and SO_2 . The system must be able to withstand SO_2 and H_2SO_4 corrosion in the

700°C range, and HI and I₂ corrosion in the 450°C range. This is a very demanding materials problem. Development of new membranes to separate O₂, H₂O, and SO₂ could result in lowering the reaction temperature, reducing the demands on other materials in the system.

In the area of solar-driven thermochemical water-splitting systems, cycles that lend themselves to hot/cold (light/dark) cycle are key. A conceptual example here could be a metal (Me)/metal oxide (MeO) cycle or, in general, a metal oxide redox cycle:



The elaboration of such cycles, which would involve less demanding materials properties, can be effective ways to produce hydrogen in combination with solar concentrators.

Relevance and Potential Impact

The DOE Hydrogen, Fuel Cells and Infrastructure programs in the Energy Efficiency and Renewable Energy and the Fossil Energy Programs have active development and demonstration programs for advanced hydrogen production technologies, in addition to enabling technologies such as membranes for gas separations and carbon sequestration. The proposed research supports these efforts by concentrating on the understanding of the fundamental mechanisms involved in advanced hydrogen production systems. The proposed research could lead to development of more efficient, lower cost methods for hydrogen production, with near-zero emissions.

Expected Impact and Time Scale

The proposed research direction looks toward basic research with practical implementation, perhaps 20 years in the future, as it is likely that low-cost fossil hydrogen production methods will dominate commercial production in the U.S. over the next few decades.

HIGH-CAPACITY HYDROGEN STORAGE FOR DISTRIBUTED ENERGY OF THE FUTURE

EXECUTIVE SUMMARY

Hydrogen has been proposed as the future low-polluting energy carrier. Nearly every energy-related application of hydrogen requires a safe and efficient hydrogen storage technology, especially in transportation, where there are serious weight and volume constraints. In fact, stagnation of the hydrogen storage technology near its present stage would require profound changes in attitudes toward transportation and significantly obstruct the prospects of a hydrogen economy. A new paradigm is required for the development of hydrogen storage materials to facilitate a hydrogen economy.

Hydrogen may be stored as a compressed gas, a cryogenic liquid, or as a hydrogen-rich solid. The first two approaches require substantial energy expenditures. Therefore, improved energy efficiency of hydrogen compression and liquefaction is desired.

Over the past three decades, solid-state hydrogen storage has involved nearly exclusively metals and metallic alloys, where the metal matrix is expanded and filled with hydrogen atoms located in interstitials. Capacities of two hydrogen atoms per metal atom have been demonstrated. However, the metal matrices consist of relatively heavy elements, such as Ti, La, Ni, etc., and storage capacities usually do not exceed 2 wt% hydrogen. Few, if any, options to modify the properties of conventional hydrogen storage alloys remain unexplored. A material approaching the required volumetric and gravimetric capacity, at reasonable temperatures and pressures, has not been discovered.

Lightweight metals, such as Li, Be, and Mg, can form high-capacity binary hydrides. However, they release hydrogen at 300-600°C, or are toxic. Carbon-based hydrogen storage has not achieved its initial promise. Experimental results are controversial and irreproducible, and significant storage is only realized at cryogenic temperatures in combination with high pressure. Such conditions are not practical for general transportation.

The ultimate hydrogen storage compound is methane, where four hydrogen atoms surround a single carbon atom. However, methane is gaseous, and the nature of the hydrogen-carbon bond does not allow easy dehydrogenation and is nearly impossible for direct rehydrogenation.

Novel materials [e.g., alanates (aluminumhydrides) and borohydrides], where a metal or a metalloid atom is surrounded by four to six hydrogen atoms forming a complex negatively charged anion, mimic methane and may provide a much needed breakthrough in solid-state storage of hydrogen. Their hydrogen capacities are high (from ~10-18% by weight), but multiple basic issues related to their hydrogen storage properties must be addressed. To date, even the atomic structures of many complex hydrides are either unknown or have been determined with insufficient accuracy. On the other hand, the nature of complex hydride solids (i.e., the ionic bonding of hydrogen-rich anions with various cations) opens a way for precise chemical substitutions in the cation sublattice, thus bridging the gap between hydrogen-poor intermetallic hydrides and hydrogen-rich LiH, BeH₂, and MgH₂. It is in this area that a significant research program is proposed.

Summary of Research Direction

Compressed storage of hydrogen is presently certified for use with 5,000 psi tanks. Research and development continues, which may result in future certification of 10,000 psi tanks. It is not certain whether higher pressures could be achieved practically and safely. This technology results in 7-10% energy lost during the compression.

Liquefied hydrogen production is an existing technology. However, energy requirements are presently too high (approximately 30% energy is lost during the liquefaction). Furthermore, cryogenic tanks are inconvenient and costly, and cryogenic storage of hydrogen has intrinsic hydrogen boil-off losses.

Over 40 years of research in conventional metal hydrides, such as LaNi_5 , ZrNi_2 , TiFe , and related alloys did not produce a material capable of reversibly storing more than 2 wt% of hydrogen. Regardless of virtually limitless possibilities to modify alloy chemistry and microstructure, no further improvements are in sight.

Binary hydrides of several light metals, such as MgH_2 (7.7 wt%), LiH (~12 wt%), and BeH_2 (~18 wt%), could provide sufficient hydrogen storage. However, hydrogen can be released only at high temperature (300-600°C), or the material is highly toxic (BeH_2). Chemical and structural modifications without capacity loss are severely limited and only minimal improvements can be envisioned.

Complex hydrides offering high-hydrogen capacities include: $\text{Al}(\text{AlH}_4)_3$ (10 wt%), LiAlH_4 (~10.5 wt%), NaBH_4 (10.6 wt%), Li_3AlH_6 (11.1 wt%), LiBH_4 (18.3 wt%), and others. To date, 7.6 wt% hydrogen release has been demonstrated for LiAlH_4 (5.1 wt% at room temperature plus 2.5 wt% below 150°C). The entire hydrogen content of $\text{Al}(\text{AlH}_4)_3$ is available below 100°C. The actual structures of a number of ternary and majority of multicomponent complex hydrides and their hydrogen storage behavior remain unknown and unexploited. Basic research effort to explore hydrogen storage properties of complex hydrides is virtually nonexistent, except for some recent work on the relatively low capacity NaAlH_4 , which contains 7.4 wt% hydrogen total.

New Scientific Opportunities

While design of a solid with 25 wt% hydrogen or more appears unfeasible (the four-coordinated carbon stores 25% hydrogen in methane), light metal-based complex hydrides with 10-18 wt% hydrogen exist. Hydrides where four to six hydrogen atoms coordinate a single metal or metalloid atom, thus forming complex $[\text{MeH}_n]^{p-}$ anions, are especially promising. Novel hydrogen-containing solids based on light elements should be engineered, synthesized, and fully characterized. This effort may include partial or complete substituting on the cation sites or exploring the feasibility of creating a variety of different kinds of anions (both in chemical composition and structure) stabilized by lightweight counterions. Thus, studies of the phase diagrams, structures, and chemical and physical properties of new hydrides are especially important. New materials chemistries could be designed, which should facilitate high hydrogen storage capacities coupled with acceptable dehydrogenation and hydrogenation pathways. Major emphasis should be placed on solids with total hydrogen content 10% by weight or more.

Bonding states of hydrogen in novel solids are different from conventional metallic hydrogen absorbers, and understanding of hydrogenation-dehydrogenation transformations at length scales from 10^{-1} to 10^3 nm has emerged as a complex fundamental problem. Especially intriguing is self-assembly of $[\text{MeH}_n]^{p-}$ anions,

which occurs in the solid state. The in-depth understanding of the mechanisms of the solid-state transformations occurring during the dehydrogenation and rehydrogenation of complex hydride solids is critical if satisfactory reversibility of hydrogen in this broad class of materials is ever to be achieved. State-of-the-art characterization of crystalline, nanocrystalline, and amorphous solids is essential because it is the only reliable way to establish the structure and intrinsic properties of hydrogen-containing solids and correlate them with their hydrogenation-dehydrogenation behavior. Although thermodynamics favor hydrogenation of complex hydrides, this has been achieved in the past via solvent processes and at high hydrogen pressures.

An issue in hydrogen storage employing complex hydrides, which requires considerable basic research, is overcoming high hydrogenation pressures. Often, hydrogenation and dehydrogenation kinetics are limiting steps. Conventional wisdom to overcome kinetic limitations calls for increased temperature, but this requires a further increase of hydrogenation pressure. Other forms of energy (e.g., mechanical, electromagnetic, sound, etc.) should be explored to improve kinetics.

Apart from gravimetric and volumetric capacity, the critical issue for novel materials to be considered for hydrogen storage and distribution is the reversibility of hydrogen release and uptake. Since in many cases it is easier to develop a method for hydrogen extraction than it is to recombine the resulting residue with hydrogen, various experimental approaches to direct solid-state synthesis of complex hydrides from elements should be studied in detail. Kinetics of solid-state transformations leading to breakdown and formation of complex $[\text{MeH}_n]^-$ anions should be explored and understood before hydrogen delivery and recharging could be controlled with the required precision. Intimate combination of the first principles theory with the state-of-the-art experiment is likely the most feasible way to design ultra high capacity hydrogen-containing solids. Prior extensive studies of the conventional intermetallic hydrides fully support the notion that the processes of the absorption and recovery of hydrogen are controlled by the thermodynamic properties of materials, complex hydrides included. Recent significant improvements of the computational methods for *ab initio* calculations of the thermodynamic and electronic properties of intermetallic compounds should be extended and applied to complex hydride materials.

Relevance and Potential Impact

The DOE Hydrogen, Fuel Cells and Infrastructure programs in Energy Efficiency and Renewable Energy and the Fossil Energy Programs have active development in fuel cells intended to be served by hydrogen in the hydrogen economy. Without a practical storage method, however, the hydrogen economy is unlikely to become a reality.

Estimated Time Scale

The proposed research could lead to development of effective hydrogen storage methods. The proposed research direction will require concerted efforts extending well over 10 years.

NOVEL MEMBRANE ASSEMBLIES

EXECUTIVE SUMMARY

Membranes that conduct hydrogen ions and oxygen ions, either alone, in combination, or together with electrons, are essential components of a broad range of energy conversion devices and fuel-conditioning systems, and play a role in nearly every energy storage scenario. The required combination of properties for these membranes, including a useful temperature range of operation, high conductivity, extreme stability, and economy, is rarely if ever achieved. Practical operating conditions may impose undesirable materials selections for the complementary system components, such as platinum catalysts below 200°C or expensive ceramics above 600°C. It is precisely in this 200-600°C temperature range that functionally useful membranes are yet to be discovered. The essential difficulty is that fundamental theories to date are inadequate for the prediction of the physical and chemical properties of single-phase, composite, and, particularly, nanocomposite membranes, their adjoining electrode materials, and their interfaces. While a complex and very challenging task, the development of such predictive theories, together with experimental exploration and verification, could dramatically accelerate the rate at which practical discoveries can be expected that have a beneficial impact on energy technology.

The benefits of novel membranes and membrane/electrode assemblies (MEAs) may be appreciated by considering the following examples. The operating temperature, efficiency, and catalytic activities of a PEMFC is limited by the dependence of the hydrated proton [i.e., $\text{H}(\text{H}_2\text{O})_n^+$] on the water content of the membrane polymer. Polymer and polymer/inorganic composite membranes of exclusive, high proton conductivity, but independent of humidity in the temperature range of 100-200°C, may enable variants to the PEMFCs with higher tolerance of anode catalyst to carbon monoxide poisoning. Thermal management would be significantly simplified, and parasitic losses associated with air pressurization could be reduced or avoided altogether.

For solid oxide fuel cells (SOFCs), reducing the temperature to 300-600°C with the accompanying development of effective oxygen and fuel electrodes would allow dramatic cost reductions for electrical interconnects and for the balance-of-plant (BOP). It would extend the domain of use of SOFCs to smaller residential or even mobile units, where bottoming turbine cycles are not indicated, operating directly on natural gas, fossil fuels, alcohols, or hydrogen.

Novel membrane assemblies must be sought to reduce the polarization resistances at membrane-electrode interfaces that limit the overall electrolytic device performance. In particular, novel membranes assemblies must facilitate: (1) the reduction of oxygen in fuel cells cathodes, (2) the oxidation of hydrogen or direct oxidation of carbon-containing fuels in fuel cell anodes, and (3) the synthesis of pure hydrogen or the reforming of carbon-containing fuels to hydrogen.

In conclusion, novel organic or inorganic membranes and their composites, assembled with high-performance electrodes and targeted for operation in the 200-600°C range, will lead to a new generation of electrochemical devices that are exceptionally effective in the energy conversion and utilization sector. Basic research can accelerate their development by stimulating the relevant theoretical studies in combination with materials experimentation, particularly in the area of nanocomposite membranes.

Summary of Research Direction

Membranes that conduct hydrogen ions and oxygen ions, either alone, in combination, or together with electrons, are essential components of a broad range of energy conversion devices, fuel-conditioning systems, and play a role in nearly every energy storage scenario. Most prominent among these are the fuel cells, of which the PEMFC and the SOFC are the target of much commercial development. Yet broad deployment of these fuel cells, which would be ideally suited to a hydrogen economy and to its fossil fuel transition phase, is hindered by the present nature of the membrane and its electrodes. The required combination of properties for these membranes, including a useful temperature range of operation, high conductivity, extreme stability, and particularly economy, is rarely if ever achieved. Practical operating conditions impose undesirable materials selections for the complementary system components, such as noble metal catalysts below 200°C and ceramics above 600°C. It is precisely in this 200-600°C temperature range that functionally useful membranes are yet to be discovered. The essential difficulty is that fundamental theories to date are inadequate for the prediction of the physical and chemical properties of single-phase, composite, and particularly nanocomposite membranes, their adjoining electrode materials, and their interfaces.

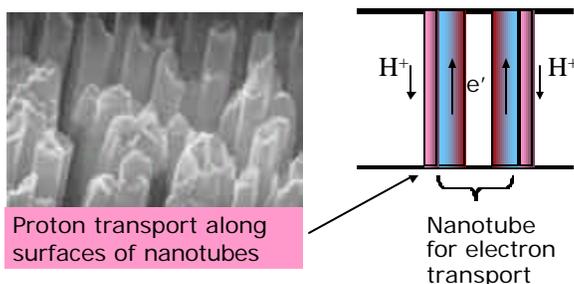
PEMs rely on a hydronium-based transport mechanism that requires liquid water within the membrane and limits the fuel cell operating temperatures to less than 100°C, unless operated at elevated pressures. The pressurized perfluorosulfonated ionomer PEM and its variants lack the properties to operate much above 140°C. Humidification of the membranes is required to maintain the water content and conductivity of the membranes. Even at operating temperatures as high as 140°C, the PEM fuel cell is quite susceptible to carbon monoxide poisoning and is most effective when operating on pure hydrogen. The low operating temperature reduces the PEMFC's utility for combined heat and power (CHP) applications, but the high power density of the PEM fuel cells make them well suited for automotive applications when operating on pure hydrogen. The high power density is a result of high catalytic activity at both electrodes and the development of highly efficient systems for thermal management combined with product water removal. Hydrogen fuel utilization (as high as 99%) and high efficiency have been achieved in PEM fuel cells operating at atmospheric pressure. Pressurized fuel cells typically sacrifice as much as 20% of the available power pressurizing the air for the cathode.

SOFCs offer promise for a clean and highly efficient system for chemical-to-electrical energy conversion when operating on fossil fuel. At 800-1000°C in a combined cycle, efficiencies of over 80% can be projected. Their fuel flexibility, from carbon-containing fuels to hydrogen, makes them well suited for the transition to a hydrogen economy. The high operating temperature of SOFCs is currently required for sufficiently fast electrode reactions (oxygen reduction and fuel oxidation) near the membrane-electrode interfaces and for fast ionic transport across the electrolyte membranes. However, this high operating temperature is at the same time the source of a range of problems, including necessity of limited and uneconomic component and material choice, complex system designs, slow cold start, and limited deployment. Accordingly, the cost of the current SOFC systems is still prohibitive for broad commercialization. To be economically competitive, both the cost of materials and the cost of fabrication for SOFC systems must be dramatically reduced. To achieve this, the SOFC operating temperature must be significantly reduced. At sufficiently low temperatures, interconnects, heat exchangers, and other structural components can be fabricated from much less expensive materials. Further, as the operating temperature is reduced, many technical difficulties can find easy solutions, system reliability and operational life increase, and the possibility of using SOFCs for a wide variety of applications becomes possible.

The essential grand challenge is to design ionic and mixed-conducting membranes with high conductivity, stability, and selectivity over a broad temperature range, especially temperatures below 600°C. Of particular interest are membranes transporting one or more of the following charged defects: proton, oxygen vacancy, oxygen interstitial, electron, electron hole, and OH. Such membranes must be combined with anodes and cathodes of high catalytic activity for oxygen redox reactions, for direct oxidation or reforming of hydrocarbon fuels, and for synthesis of cleaner fuels. This can only be achieved if relevant theory development combines effectively with experimental investigation. In particular, considerable potential for innovation, both on the theory and practical side, exists in the study of nanocomposite membranes and transport along their internal interfaces, as for example shown in Figure 5-1.

Similar concepts may be applied to create nanocomposite membranes that exhibit exceptionally high selectivity for molecules rather than ions. Such composite membranes may lead to revolutionary means of fast gas separation that in turn may profoundly impact on hydrogen and other gas separations beneficial to fuel cells and hydrogen production.

Proton-Electronic Membranes



New Scientific Opportunities

While the quantum effects in optical and electronic processes have been extensively studied, transport of ionic species and catalytic reactions at nanoscale are yet to be examined. A fundamental approach to the ionic and electronic transport in nanoscale composite membranes, such as the one sketched in Fig.1, involves both phenomenological theory development as well as *ab initio* calculations.

- Hydrogen separation/purification
- Electrodes for fuel cells based on proton conductors

Figure 5-1. Conceptual example of a possible nanocomposite membrane.

These are used to obtain insight into mechanisms of ionic and electronic transport along or near interfaces in nanocomposites where the surface of the particulates, such as carbon nanotubes, have been functionalized with organic or inorganic adducts, and where the carbon may transport electrons. A membrane with rapid transport of both electrons and protons may be used for hydrogen separation, purification, and electrosynthesis of cleaner fuels.

For ceramic membranes, predictive theories, such as advanced molecular dynamics treatments, must be developed that clarify the rate limits, temperature dependence and mechanisms of ionic conduction, particularly for oxygen ions and protons. This will facilitate both novel membrane design and electrode formulations.

It is proposed: (1) to explore ionic and mixed transport with both phenomenological theory development as well as *ab initio* calculations; (2) to combine these theory developments effectively with parallel experiments; (3) to characterize transport mechanisms and other emergent phenomena relevant to ionic transport using the advanced facilities, such as high resolution electron microscopy, neutron scattering, and advanced light sources, available at the DOE National Laboratories; (4) to design rationally nano-structured

membranes with rate of ionic and electronic transport several orders of magnitude higher than any existing membranes in the 200-600°C range; (5) to fabricate nano-structured membranes exploring templating and self-assembly processes; and (6) to seek effective electrodes that in combination with the novel membranes lead to economic energy conversion and utilization devices in the 200-600°C range.

Relevance and Potential Impact

The novel membrane assemblies that result from the proposed work would have an impact most directly on the applied DOE programs in Fossil Energy, Energy Efficiency, and Renewable Energy. These membrane assemblies include:

- *proton membranes* for PEM fuel cells, hydrogen separation and purification, hydrogen sensors;
- *oxygen ion membranes* for low-temperature SOFCs, electrolyzers, partial oxidation and reforming of hydrocarbon fuels, contaminant removal, and oxygen sensors;
- *mixed-conducting membranes* for hydrogen separation/purification, oxygen separation, reforming/partial oxidation of hydrocarbons (e.g., methanol); and
- *membrane-electrode assemblies (MEAs)* for increased efficiency and reduced cost of fuel cells, batteries, hydrogen separation/purification, oxygen separation, reforming/partial oxidation of hydrocarbon fuels, contaminant removal, gas sensing, and other processes relevant to energy storage and conversion.

Estimated Time Scale

10-20 years for full theory development, with first practical payoff within 5–10 years.

DESIGNED INTERFACES

EXECUTIVE SUMMARY

The utilization of hydrogen- or carbon-containing fuels in electrochemical systems depends critically on the properties of interfaces that need to fulfill specific and often conflicting functions. Among these functions are structural, dimensional and chemical stability; rapid electron, ion, and mass transfer; and catalysis or electrocatalysis; all under a wide range of temperature, temperature changes, and gas partial pressures variations. This multitude of interactive factors vastly complicates the fundamental understanding of interface processes in electrochemical energy conversion devices and hinders the development of practical and economic fuel cells. The direct predictive first-principles computation of the responses of an electrochemical interface to input variables which includes factors such as chemical composition and ionic and electronic conduction, is likely to remain intractable. Yet, progress in this field could be dramatically accelerated if means were created to combine phenomenological and computational interface theory with experimental data. The neural network approach to this complex problem is envisioned to offer the possibility of pointing the way to novel interface concepts, of which the expected properties may be at least qualitatively if not quantitatively predicted.

As improved theories mature, and the reliable experimental database expands, the predictive capability of the neural net can be expected to expand from small excursions from known behavior to more speculative concepts. It is likely that nature of the various network nodes and their transfer functions will have to be modified from current models to be able to deal with the mix of theory and experiment. The construction of a dependable neural net for the expected properties of various interfaces in electrochemical systems can be invaluable in the design of such interfaces at all levels.

Summary of Research Direction

The neural network approach to problem solving evolved from attempts in the 1930's to understand and mimic cognitive processes. A network topology is constructed, inspired by the structure of biological neurons and their interconnections, consisting of input nodes that receive data; the transmission of these input data to hidden nodes via weighted interconnects; the evaluation of the all-weighted input data by a hidden neuron layer using various activation functions, which may be linear, non-linear, binary, or probabilistic; and an output neuron layer which produces the results by applying again some activation function to the weighted sums of the outputs of the hidden nodes. The process is schematically illustrated in Figure 5-2.

The “knowledge” resides in the weights of the interconnects. Thus, adjusting the weights w_{ij} to reach a known output from a defined input constitutes learning.

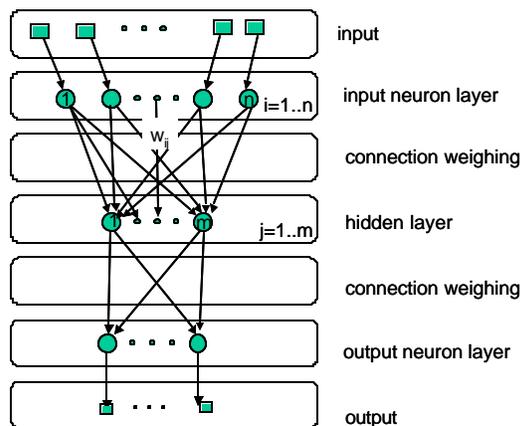


Figure 5-2. Schematic of the basic neural network. All “input neurons” i are connected to all “hidden neurons” j by an interconnect ij , of which the importance (*i.e.* the weight w_{ij}) is adjustable.

Neural networks in combination with fuzzy logic have been used successfully in optical pattern and in speech recognition. They have been applied to an increasing range of applications as diverse as banking failure prediction, mortgage credit approval, process management and control, hotel room pricing, and medical diagnosis. In materials development, the neural network approach has been successful (e.g., in the design of improved nickel-based superalloys for airplane engines and for power plant turbines).

New Scientific Opportunities

A neural network approach to the design of low-impedance interfaces and electrode surfaces with high electrocatalytic activity has not yet been attempted. The construction of such a neural network would require innovation in the integration of existing and new theory of electrochemical interfaces with extensive reliable data sets obtained from well-characterized interfaces. Initially, problems may be formulated such as the alloying of a nickel surface to reduce its sensitivity to sulfur poisoning, minimally compromising its catalytic activity for hydrocarbon oxidation.

Relevance and Potential Impact

The potential impact of a predictive neural network approach to design electrochemical interfaces would be far-reaching, providing accelerated development of practical fuel cell systems, hydrogen generators, and related devices under active consideration in the DOE programs on Fossil Energy, Energy Efficiency, and Renewable Energy.

Estimated Time Scale

This new enterprise may reach maturity in 10-15 years, with significant practical results generated as it evolves.

Transportation Energy Consumption

**Integrated Quantitative Knowledge Base for Joining of
Lightweight Structural Materials for
Transportation Applications**

Vehicular Energy Storage

Fundamental Challenges in Fuel Cell Stack Materials

Integrated Heterogeneous Catalysis

**Thermoelectric Materials and Energy Conversion Cycles
for Mobile Applications**

Complex Systems Science for Sustainable Transportation

INTEGRATED QUANTITATIVE KNOWLEDGE BASE FOR JOINING OF LIGHTWEIGHT STRUCTURAL MATERIALS FOR TRANSPORTATION APPLICATIONS

EXECUTIVE SUMMARY

Although the use of new strong light-weight alloys, composites and other materials in vehicles will reduce consumption of fuel and reduce emissions, the maximum benefit from the use of these materials cannot be achieved without a detailed, quantitative knowledge base of how materials transform and behave under the extreme conditions characteristic of joining processes. Spatial and temporal gradients of temperature, composition and structure are a common result of materials joining. The component physical processes depend strongly upon the materials system and the joining process. While various component physical processes of materials joining have been modeled individually in metallic and, to a far lesser extent, nonmetallic systems, integration of these individual models is needed to predict the results of joining. This is typically a very highly complex process. For example, in metallic systems, the component physical processes in fusion welding include heat transport from a source such as a laser beam, a plasma arc, or an electron beam to the materials being joined; the fluid flow, heat transfer and mass transfer in the liquid region; the absorption and desorption of gases; the vaporization of alloying elements; solidification and phase selection processes; and solid-state transformations. Each of these processes has been modeled with various degrees of quantitative fidelity, but no integrated model exists. In another example, for the joining of certain important ceramics, a process such as diffusion bonding may be used where thermal diffusion and interfacial phase formation are important to joint strength and toughness. Joint interfacial reactions also play an important role in affecting joint integrity in other materials. The ability to incorporate advanced materials into future transportation systems will be greatly enhanced by an integrated predictive capability for joint geometry, microstructure and chemical composition to address such critical issues as strength, reliability, manufacturability and cost of the structure that contains the joint. The broad scope of this quest will require contributions from several scientific disciplines and will require coupled experiments and predictive modeling. During integration of the various component models, new scientific opportunities will arise at the crossroads of basic and applied sciences. Direct benefits of the work will be the easier incorporation of advanced materials into transportation systems with attendant lower costs and improved reliability in mass-produced structures. Alternate repair strategies can also be easily explored.

Summary of Research Direction

Defect free, structurally sound and reliable joints are often fabricated by empirically adjusting variables through trial and error. Although this practical approach often produces an acceptable end result, it ignores the potential competitive technological advantage that is attainable through fundamental understanding of the underlying science. Furthermore, the ranges of variables chosen empirically do not always produce optimum results.

Predicting and controlling joint geometry, composition, structure and properties are difficult because the joining processes are highly complex and the fabricated joint is compositionally and structurally non-homogeneous. For example, in metallic systems, the component physical processes in fusion welding include heat transport from a source such as a laser beam, a plasma arc, or an electron beam to the materials being joined; the fluid flow, heat transfer and mass transfer in the liquid region; the absorption and desorption of gases; the vaporization of alloying elements; solidification and phase selection processes;

and solid-state transformations. In another example, for the joining of certain important ceramics, a process such as diffusion bonding may be used where thermal diffusion and interfacial phase formation are important to joint strength and toughness. Joint interfacial reactions also play an important role in affecting joint integrity in other materials. In addition, the fabricated joints typically contain spatial gradients of composition, structure and properties. These special features of the joints, and the diversity of the simultaneously occurring component physical processes in joining, make the prediction and control of joint properties a highly complex venture.

Recent advances in computational hardware, software and numerical models have made many complex processes tractable. In the field of fusion welding, significant progress has been made in the numerical modeling of several important component physical processes. These include formulation and testing of models of heat transfer, fluid flow and thermal cycles, mostly for simple geometry; numerical simulation of grain growth and phase transformations in some alloys; and calculation of residual stress and deformations. In addition, numerical models to avoid formation of simple defects such as porosity have also been proposed and tested. However, many of these models are fairly complex and computationally intensive. Furthermore, the component physical processes have not been synthesized into a single comprehensive model. The ability to predict joint geometry, microstructure, chemical composition and properties will greatly enhance the quality, reliability and serviceability of structures that contain the joints.

The broad scope of this quest will require contributions from several scientific disciplines and will require coupled experiments and predictive modeling. The constituent sub-models may or may not be phenomenological in nature, depending on the materials system and complexity. For example, a phenomenological approach is often adapted for the representation of heat transfer, while a neural network type model has been more successful for the prediction of mechanical properties of joints. During integration of the various component models, new scientific opportunities will arise at the crossroads of basic and applied sciences. Direct benefits of the work will be the easier incorporation of advanced materials into transportation systems with attendant lower costs and improved reliability in mass-produced structures. Alternate repair strategies can also be easily explored.

New Scientific Opportunity

As a result of significant advances in computational hardware and models, opportunities now exist to integrate numerous important constituent models into a usable knowledge base for predicting the response of new materials systems to a selected joining process. While many component physical processes of materials joining have been modeled individually in metallic and non-metallic systems, integration of these individual models is needed to predict the results of joining, typically a very highly complex process. The interdisciplinary nature of the task will require synthesis of knowledge from various disciplines such as plasma physics, thermodynamics, chemistry, materials science, transport phenomena, and various engineering fields such as mechanical, chemical and electrical engineering.

Relevance and Potential Impact

An important component to achieve energy efficiency in the transportation sector is the replacement of traditional structural materials by lighter and stronger materials, which results in direct reduction in energy use. Although the proposed research direction in joining will benefit the transportation sector, its impact will also be realized in all segments of applied energy programs where joining of structural materials is

important. These applied energy programs include fossil, nuclear, energy efficiency, renewable energy and fusion.

Estimated Time Scale

As component models are synthesized into large comprehensive models, there will be progress toward a science-based prediction and control of composition, structure and properties of joints. Achievement of this challenging but realistic goal, an important milestone in the advancement of joining technology, is well within the reach of the research community, provided adequate resources are available. It is expected that the benefits of the work will be fully realized in several decades.

VEHICULAR ENERGY STORAGE

EXECUTIVE SUMMARY

High energy-density storage materials will be needed if strategic energy goals are to be satisfied for the transportation sector. Unlike stationary demands, mobile requirements dictate both high volumetric and gravimetric energy density. At present, the transportation sector is almost totally dependent on petroleum fuels for its energy needs as they satisfy the principal need of high energy density. Attempts to replace petroleum fuels with other sources of readily transportable and abundant energy have met with limited success, due principally to the inability to store on-board a vehicle, sufficient quantities of the alternatives to provide vehicle performance that is competitive with petroleum fuels.

Among the candidate energy carriers, hydrogen and electricity are two that can satisfy the abundance requirement but which are low in energy density.

Hydrogen sorbents and hydrides may offer a means of obviating high pressures and/or low temperatures to attain higher volumetric and gravimetric energy densities. In fact, metal hydrides are presently capable of volumetric densities greater than that of liquid hydrogen, but fall short of the requirements for high gravimetric density. In order to satisfy gravimetric energy density requirements, sorbents based on low atomic number (Z) materials will need to be used. Our present knowledge of known stable hydrides, based on low Z materials that serve as suitable candidates for gravimetric and volumetric hydrogen storage, is limited to systems with thermodynamic and kinetic barriers that are too high to be of use to the transportation sector. Such systems may also suffer from irreversible hydrogen cycling limitations. Systems based on complex hydrides can offer possibilities for high volumetric and gravimetric storage but are poorly understood. For example the NaAlH_4 system, which is closest to engineering realization, has multistep hydride/dehydride reactions with differing kinetic and thermodynamic values. These are only realized in the presence of a dopant (catalyst) with a poorly understood role. This circumstance makes the understanding of hydride materials an imperative if new materials are to be developed for attaining the goal of hydrogen-fueled vehicles.

In the near term (5-10 years), it is expected that batteries possessing enhanced energy and power densities as well as lifetimes will be needed to enable hybrid/electric vehicles having performance characteristics comparable to conventional internal combustion (IC) engine/petroleum fueled vehicles. Present state-of-the-art technology using Li batteries offers the highest energy densities [twice that of NiMH batteries that are used in hybrid and electric vehicle (EV) technology] and cycle life, but the components, including cathode, electrolyte and separator, are costly. Provided improvements to energy density over current Li technology can be made, batteries might still be used as the primary power source for a pure electric vehicle. In any event, high energy density systems with high cycle life will still be necessary. Even for hybrid technology, batteries are a vital part of the overall power system for hybrid vehicles that utilize regenerative braking. Candidate systems based on Li battery technology offer the highest known energy densities available, but these systems still fall short of automotive design goals that would make such vehicles competitive with petroleum-based systems. An effort to better understand and design suitable cathodes, anodes and separators for Li batteries would benefit the transportation sector as well as the area of portable electronics.

Summary of Research Direction

A research direction based on the study of the thermodynamics, kinetics and phase stability of energy storage materials is proposed. These basic scientific issues are germane to the two specific areas we highlight below for hydrogen storage materials and batteries.

Hydrogen Carriers. The DOE's technical targets of 6 wt% (7.2 MJ/kg energy density) gravimetric storage and 1100 Wh/L (4 MJ/L energy density) volumetric storage for hydrogen systems for transportation applications illuminate the scientific and technological gap in establishing fuel cell viability for commercial markets. The current state-of-the-art energy storage technology can be categorized broadly into physical and chemical storage. Physical storage would consist of cryogenic systems and high-pressure tanks. Liquid hydrogen and compressed hydrogen systems presently fall short of the minimum performance goals ($>6\text{MJ/kg}$ and $>6\text{MJ/L}$) sought after by the transportation sector and fall far short of the ultimate technological gravimetric and volumetric target goals ($>12\text{MJ/kg}$ and $>12\text{MJ/L}$). From a refueling standpoint, these systems are extremely inefficient. For example, hydrogen liquifaction consumes an equivalent of 30% of the energy density of liquid hydrogen itself (to get to 20 K). Also, multistage compressors are required to achieve the high pressures (690 bar or 10,000 psi) for the compressed hydrogen systems that are being developed.

Chemical storage systems, which would include hydrogen sorbents or hydrides, may offer a means of obviating these inefficiencies by allowing high gravimetric and volumetric energy densities at non-cryogenic temperatures. For example, MgH_2 has a density of 1.45 g/cc or 0.11 g(H_2)/cc. This material thus has a gravimetric density of 7.66 wt% (9 MJ/kg of MgH_2 , materials basis only) and 110 kg/m³ (13 MJ/L). Unfortunately, Mg dehydrides at too high a temperature to be a practical source of hydrogen for vehicular applications (~600 K). To work with presently available fuel cell proton exchange membranes, the desorption temperature would need to be closer to 350 K. In any event, rehydriding is also problematic for MgH_2 . At present, Ti-catalyzed NaAlH_4 shows potential as a storage material but again falls short in gravimetric density (5.6 wt% or 6.7 MJ/kg materials basis).

Hydrogen physisorption might also work for storage applications but, to be of use for vehicular applications, will require an adsorption enthalpy of 20 to 40 kJ/mole (~200 to 400 meV), if sorbent dehydriding/hydriding near ambient temperature and moderate pressures is to be achieved. In addition, physisorption will require effectively high surface area materials that have a suitable number of adsorption sites to accommodate molecular hydrogen.

If the criterion of high volumetric density was the only concern, a number of metal hydrides would work. The concomitant requirement of high gravimetric density restricts the possible hydride candidates to a limited portion of the periodic table or alloy/chemical constituent components. To date, though, few systematic efforts have looked into suitable candidate materials. The payoff from systematic efforts can be seen when considering that NaAlH_4 was discarded as a candidate material because this material was regarded as too volatile and with too low a melting point before hydrogen was released. Over 20 years later, however, it was discovered that a Ti catalyst added to NaAlH_4 could promote the kinetics of dehydriding while the material was still in the solid state, bringing it to the point of engineering viability [B. Bogdanovic and M. J. Schwickardi, *J. Alloys Compd.* 253, 1 (1997)]. At present however, the role of this catalyst is still unknown.

The choice of candidate sorbents or hydrides can be reduced further on the basis of free energy and heat of formation data (thermodynamics) to systems that can operate over temperatures of engineering interest. Applying information gleaned from the JANAF Thermochemical Tables is helpful but understanding multicomponent systems may also require information not yet available but possibly calculable. For instance, Miedema heats have been used to understand the behavior of AB_5 hydrides, and their utility in other systems should be established in order to limit the phase space of elements and compounds deemed suitable for vehicular applications. Furthermore, the kinetics of dehydriding and rehydriding will also be important in addressing fuel uptake and refueling. Finally, issues related to the cycle life of the sorbent or hydride (phase stability) need to be addressed.

Batteries. Lead-acid battery technology, which was developed nearly 150 years ago, is still being used for vehicular applications. These batteries have a gravimetric density of 0.16MJ/kg and 0.25 MJ/L. Ni-metal-hydride batteries have gravimetric and volumetric energy densities nearly twice that of lead-acid, and Li batteries (0.5MJ/kg and 1MJ/L) have values twice that of NiMH. The United States Advanced Battery Consortium has set a long-term goal of 0.72 MJ/kg energy density. At present, it is difficult to imagine improving on the energy density of Li batteries unless improvements to cathodes (typically $LiCoO_2$) are found. Incremental improvements are on the horizon through partial substitution of Co by Ni yielding ~15% improvement in charge capacity (resulting from the phase stability of $LiNi_{0.8}Co_{0.2}O_2$ to retain a stable phase to discharge levels to $Li_{0.4}$). Longer term goals aimed at improving energy density in Li batteries should consist of studying Li insertion/de-insertion kinetics and phase stability of both cathodes and anodes in non-Co based materials. Also, Li-based systems have specific charge/discharge requirements requiring specialized electronics designed to control limits and rates for each cell of a battery pack. Cathodes and anodes that offer the possibility of higher robustness to high discharge rates and overcharging may allow for the simplification of Li-based systems. For instance, Li_2S -based systems demonstrate such robustness and have shown capacities as high as 0.65MJ/kg. A combination of doubling of the energy density of Li secondary (rechargeable) batteries in conjunction with robust cathode/anode systems would be the enabling factors in implementation for the transportation sector as well as offer huge benefits for other sectors like portable electronics.

New Scientific Opportunities

The issues surrounding all high energy density materials fall within the traditional scope of BES in addressing the thermodynamics (temperature), kinetics (hydriding/dehydriding and charge/discharge rates) and phase stability (cycle life) of materials. A focused basic research effort into materials of specific interest for high energy density would greatly benefit those areas with specific technological goals for vehicular applications.

Relevance and Potential Impact

The *National Hydrogen Roadmap* calls for a coordinated national program to advance hydrogen storage materials as no current technology satisfies the storage criteria of manufacturers and end-users. Current research and development efforts are cited as insufficient as storage is noted as a critical enabling element in the hydrogen cycle. While technical goals are easy to identify, fundamental improvements in hydrogen storage processes remain to be fully understood. Developing this understanding should be the long-term goal and a necessary step before the challenges of addressing technical goals is met.

Estimated Time Scale

A coordinated effort over a period of ~10 years is likely required to meet the challenges outlined here.

FUNDAMENTAL CHALLENGES IN FUEL CELL STACK MATERIALS

EXECUTIVE SUMMARY

Offering enormous potential for high-efficiency, pollution-free propulsion, fuel cells (FCs) are of great interest in the transportation sector. The PEMFC is the leading candidate for the primary power source in FCEVs, with hydrogen as the fuel and water and heat as the only by-products. SOFCs are under consideration as auxiliary mobile power units in heavy-duty trucks. While considerable progress has been made in moving FCs closer to economic viability, many major scientific and technological hurdles remain. A hand-built prototype PEMFC presently costs thousands of dollars per kilowatt. Elimination of the hurdles will allow dramatic cost reductions, which will, in turn, hasten large-scale commercialization of FCEVs.

Among the technical challenges are a variety of materials issues related to the FC stack, the array of individual cells linked in series to form a power unit. For PEM stacks the needs include cost reduction, simplified heat, air and water management; higher efficiency; and improved reliability and durability. These objectives may be achieved through research in high-temperature and low-relative-humidity membranes, modeling and diagnostics, improved cathode kinetics, base-metal CO-tolerant catalysts, and improved bipolar plate materials. For SOFC stacks the critical issues are thermochemical integrity and reliability, interconnect durability and performance, power density enhancement, and direct reformation of hydrocarbon fuels. All of these challenges can be addressed through fundamental materials research focused on new membranes, bipolar plates, electrodes, and electrolytes, coupled with theoretical modeling to accelerate their design and evaluation.

Summary of Research Direction

FCEVs represent a potent option in the portfolio for meeting the future transportation needs of the U.S. Despite significant advances in FC technology over the past few decades, however, many fundamental scientific and technological barriers stand in the way of large-scale commercialization for mobile, as well as fixed station, applications. Associated with the FC stack itself are a variety of basic materials research challenges that can be addressed by a sustained and coordinated effort. For the cost per kilowatt to be reduced sufficiently to enable widespread use of FCs and FCEVs, novel materials having improved properties for FC stacks must be discovered, developed, and understood.

New Scientific Opportunities

PEMFC stacks. In view of its advantages with respect to energy efficiency, emissions, and feedstock diversity, the PEMFC is the leading option as the primary power source in FCEVs. Fueled with hydrogen (having a spectrum of possible production methods), the PEMFC can operate at average efficiencies twice as high as today's internal combustion engines, with water and heat as the only by-products. Large-scale commercialization of FCEVs, however, will require dramatic reduction of the cost of the FC stack, which is a critical issue dependent upon groundbreaking fundamental research on a number of fronts for resolution. These include:

- High-temperature membranes. Fuel and air streams in current systems, operating at ~80°C, must have relative humidity (RH) at about 100% to maintain high conductivity in the membrane and catalyst layers. Substantially improved system efficiency (stack, and water and heat management) could be

achieved with higher operating temperature ($\sim 120^\circ\text{C}$), but a 120°C system is not feasible with available membranes because of excessive pressure and water recirculation demands. Membranes capable of sustaining ~ 0.1 S/cm conductivity at RH $\sim 25\%$ and 120°C are required. Specific research topics in this regard are (1) new proton/anion conductivity mechanisms not dependent on high RH, (2) new membranes/polymers with improved *ex situ* properties (i.e., conductivity, hydrogen/oxygen permeability, mechanical robustness) for high temperature application, (3) improved basic understanding of membrane chemical degradation in a high-temperature FC environment, and (4) studies of polymer interaction with other FC components (e.g., the effect of new ionomers in contact with catalysts on cathode kinetics).

- Stack modeling and diagnostics. Materials and stack design have been done empirically thus far. There is a genuine paucity of predictive models for flow-field and current-density distribution as well as methods to measure key component properties. Computational fluid dynamics (CFD) models have not yet had an impact on design because of excessive computation times and lack of verification. The effects of liquid water are poorly understood, the nature of flooding is unclear, and there is insufficient knowledge of water transport in diffusion media and flow fields. Relevant research topics are (1) liquid water formation and transport in porous media and through FC channels, (2) measurement of membrane electrode assembly properties (proton conductivity, gas permeance, current density, kinetics, interfacial and bulk thermal conductivities as functions of pressure), (3) novel characterization techniques that will enable broader insight, and (4) development of useful CFD models.
- Improved cathode kinetics and improved CO-tolerant catalysts. Major stack efficiency losses, causing heat rejection problems, are associated with poor cathode catalyst kinetics. There is a critical need for low-cost, non-noble metal catalysts and catalyst localization techniques. Also, anode CO tolerance also requires fundamental catalyst development.
- Improved bipolar plate materials. Currently the thickness required for carbon/polymer composite plates to have sufficient physical stability and durability is too large, resulting in volumetric energy density too low for automotive use. These high-carbon-content materials entail expensive processing and are brittle. Available metallic plates (e.g., stainless steels, titanium) are sufficiently thin (~ 0.1 mm), but noble-metal conductive coatings are needed for low contact resistance. In some cases corrosion of the plate substrate and the coating is an issue. Novel and economically feasible plate materials that overcome these challenges are imperative.

SOFC stacks. Current SOFC prototype stacks operate at $750\text{--}1000^\circ\text{C}$ and have potential as auxiliary power units functioning at high overall efficiency in mobile applications. Major challenges confronting stack performance and operation are (1) thermomechanical integrity and reliability of a complex structure, (2) interconnect durability and performance, (3) intrinsic power density, and (4) direct reformation of available hydrocarbon fuels.

These challenges can be addressed through advancements in new electrodes and electrolytes having substantially higher electrochemical activity and intrinsic power density, thus allowing for reduction in operating temperature and alleviating the challenges associated with mechanical durability and interconnect degradation. Cathode materials have improved only slowly over the past two decades, progress having been achieved through intensive semi-empirical investigations of narrow classes of materials. Rapid further advancements require a fundamental understanding of oxygen adsorption and transport in the cathode and

at the cathode/electrolyte interface. The effect of materials composition can be probed with real-time *in situ* interrogation of these surface and bulk phenomena using surface diagnostic tools, augmented by electrochemical characterization. Improved understanding of the effects of surface features and local chemistry in both real and model electrode materials can spur rational design of new cathode compositions. In addition to fundamental studies of oxygen reduction, computational chemistry can be employed to predict the effects of various materials combinations and crystal structure on the electrocatalytic reduction of oxygen. Combinatorial methods for preparing and screening samples having compositions selected with the guidance of model predictions can enable accelerated testing, evaluation, and discovery of radically improved materials. Novel compositions with optimized microstructure could be fabricated by means of emerging synthesis/deposition techniques, and possibly self-assembly of tailored porous microstructures as well, to promote high electrochemical activity. Close coupling of predictive electrochemical modeling tools with formulation and testing of new oxide electrode materials can provide fundamental understanding of the roles played by microstructural features and chemistry and speed the design of materials with better performance.

Similarly, the design of new functional anode systems must be based on an improved understanding of fuel oxidation kinetics in porous ceramic and ceramic-metal composite systems. Improved anode systems could help meet key challenges to anode performance, including the need for direct fuel oxidation or *in situ* fuel reformation and tolerance to fuel impurities. With improved electrodes, there will be an increasing need for electrolytes characterized by high ionic conductivity at lower temperatures. As outlined in the approach to electrode understanding and design, computational chemistry tools and combinatorial synthesis capability can also be harnessed to design new and better electrolyte materials.

Relevance and Potential Impact

Current industry and DOE (FreedomCar, Hydrogen, and Fossil Energy) programs are generally aimed at component and system hardware demonstration, along with core technology development for stacks or balance-of-plant. This proposed research direction on stacks through BES is aimed at addressing the more fundamental materials and surface issues governing electrochemical performance, using both experiment and modeling. The understanding of electrochemical transport through membranes and interfaces, and new materials and mechanisms developed under this program, should directly feed into the applied programs funded by DOE and industry, helping to accelerate the pace of FC penetration in transportation, and stationary applications.

Estimated Time Scale

A sustained effort in fundamental research over a period of ~10 years is likely required to meet the challenges outlined here, and enable the transition to FC powered vehicles over the next two decades.

INTEGRATED HETEROGENEOUS CATALYSIS

EXECUTIVE SUMMARY

Catalysis currently plays a significant role in the economic and strategic needs of the country. More yearly Gross Domestic Product (GDP) is produced from catalysis in the U.S. than the entire GDP of most developed nations. In particular, catalysis has and will continue to play a central role in the transportation sector, a sector that will have a considerable impact in determining our nation's future energy security. The needs for fuels synthesis and storage, for efficient fuels utilization, and for environmental mitigation of the deleterious effects of transportation on our environment are enabled through fundamental catalysis research.

The development of novel catalysts and catalytic processes for energy security applications is hampered by the lack of detailed structure-function relationships that serve to drive the development of a predictive capability for new catalyst process concepts and in catalyst materials design. Such new processes and materials will have an impact on future choices in transportation fuels and for efficient fuel utilization processes. Therefore, it should be a national priority to foster and support an integrated world-leading, vibrant and dynamic research infrastructure in catalysis. Such an infrastructure must necessarily involve highly integrated cross-disciplinary thrusts that take advantage of existing, emerging, and new structural tools; computational modeling and simulation techniques; experimental and theoretical reaction pathway modeling; and data fusion techniques that merge the output from these disparate sources into a coherent, predictive description of heterogeneous catalyst structure and activity. For example, the expected impacts of catalysis research for the transportation sector range from catalysts and processes for the abatement of lean-burn internal combustion engine exhaust in the short-term to the longer term developments directed at the rational design of catalysts that will enable the synthesis and utilization of future fuels for combustion, fuel cells, and other yet-to-be-discovered energy production concepts for vehicular and aircraft propulsion. The need to minimize the environmental impacts of any new energy production technologies also argues for a continued fundamental science research emphasis on catalytic emission control processes. Many of the short-term technological goals of the 5-10 year time frame map onto current 'FreedomCar' initiatives (DOE EE/RE). The longer term scientific goal of an integrated research infrastructure in catalysis to support the transportation sector falls to DOE's Office of Science (OS), and is the primary focus of this brief report.

Summary of Research Direction

The development of novel catalysts and catalytic processes for energy security applications is hampered by the lack of detailed structure-function relationships that serve to drive the development of a predictive capability for new catalytic process concepts and for the design of new catalyst materials. Such a predictive capability will have an impact on future choices in transportation fuels and fuels utilization processes.

A number of recent BES workshops have identified the importance of catalysis to the economic and environmental well being of the U.S., and the reader is directed to the reports that have been issued or will be issued in the near future. Historically, catalysis has been driven by the preeminence of the U.S. chemical and petrochemical industries, where catalysis is a core technology. The linkage between catalysis and transportation is crucial and will continue to be so into the foreseeable future. Catalysis is a central technol-

ogy to the current atom- and energy-efficient production of today's hydrocarbon fuels from petroleum and emerging low-sulfur diesel fuels from natural gas, the abatement of undesirable emissions resulting from the utilization of these fuels, and the synthesis of lubricants for vehicles. Catalysis also plays a central role in fuel cell technology (both low temperature electrocatalysis in polymer electrolyte fuel cells for mobile applications and catalysis of high-temperature processes in solid oxide fuel cells proposed for auxiliary power applications in heavy vehicles). In this way and in many others, catalysis will be an enabling technology for a possible future 'hydrogen economy'.

For transportation, heterogeneous catalysis is one of the key cross-cutting technologies for which the underpinning fundamental science needs are highly compelling. The focus on heterogeneous rather than homogeneous catalysis was arrived upon by the particular needs of vehicular application or the need for the very large-scale processes needed to provide for fuels of the future.

The short-term needs for catalysts in the transportation sector are at some level being partially addressed by DOE's EE/RE FreedomCar programs. For example, applied research to address the abatement of pollutants, such as NO_x and particulates from lean-burn internal-combustion engines using both catalytic and plasma-based approaches, are currently funded at some level by DOE EE/RE. Importantly, however, as pointed out in several recent National Research Council reports and reports prepared for the Office of FreedomCar and Vehicle Technology related to heavy-duty engines, the current technology options are still inadequate to allow for the introduction of these fuel-efficient engines into the U.S. economy, particularly because the pollutant targets become more aggressive entering the next decade. These reports continue to stress the need for increased investments for fundamental science that enables breakthroughs in emissions abatement to enable reductions in the energy intensity of the transportation sector.

Short- to medium-term applied research sponsored by EE/RE on the optimization of electrocatalysts for PEMFC stacks is also well underway in the U.S. Here again there are many fundamental catalysis science issues that need to be addressed to move these technologies forward. Of perhaps primary importance, however, are longer-term fundamental research needs that must be met for advanced transportation systems that are beyond the time horizons of DOE's technology offices, and fall within the boundary of DOE's OS. It is the latter longer-term catalysis research that the topical team focused on.

Broad areas (both short- and long-term) of catalyst science needs for advanced transportation systems were identified:

- catalysts for the generation of H_2 (either photocatalysts, electrocatalysts, or thermocatalytic systems);
- chemical and biocatalysts for the generation of liquid fuels from natural gas and biomass;
- catalysts for the synthesis of tailored, high-energy-density naphthenic fuels for the aviation sector;
- catalysts for reducing emissions from high-efficiency lean-burn combustion engines;
- catalysts to enable rapid H_2 uptake and release in high-energy-density hydrogen storage materials; and
- electrocatalysts, particularly oxygen reduction catalysts having improved O_2 reduction kinetics, for improved fuel cells for transportation.

Because catalysis science is a crosscutting area, it is not surprising that the Fossil Energy and the Distributed Energy, Fuel Cells, and Hydrogen Topical Groups also addressed several of these areas in more detail, and those interested in the role of catalysis in those topical areas should refer to those sections of this workshop report.

Today, it is not uncommon for practitioners of homogeneous catalysis to have considerable knowledge of the orientation of ligands, bound substrates, intermediates, or products to a metal center using a combination of nuclear magnetic resonance, infrared, and other spectroscopies. If this complex is not *the* active catalyst but rather a precatalyst, it is often very closely related compositionally or structurally to the active catalyst. This information allows for a rapid assessment of the influence of the subtle changes in steric and/or electronic structure effects, not only by rational modification of the ligands on catalyst reactivity, but also by more detailed theoretical modeling and simulation of the molecular and electronic structures of the active catalyst. Structural knowledge of enzymes has led to bioinspired synthetic homogeneous model systems that in turn, have helped to guide interpretation of the spectroscopic signatures observed during complex enzyme catalysis. The field of heterogeneous catalysis does not share these luxuries afforded by a detailed knowledge of the local structural details of a heterogeneous catalyst.

The last decade of heterogeneous catalysis research has led to advances in theory and experiment that have moved the field of catalysis incrementally closer to the much sought-after *de novo* design of heterogeneous catalysts. More recently, high throughput experimentation has improved the rate at which catalyst compositions may be varied and tested, driving the data-driven design of catalysts forward. Concepts of homogeneous- and bio-catalysis have inspired new heterogeneous catalyst synthesis efforts. New methods of catalyst characterization have emerged that allow more insights into catalyst reactivity. Theoretical approaches have been able to provide hints and guidance to some problems in catalysis, albeit based upon scant structural evidence. These are all efforts that have been ongoing, and have been providing glimpses of the workings of active catalysts.

New Scientific Opportunities

The continued lack of *detailed* knowledge of catalyst structure under realistic operating conditions has hindered catalysis science from making great strides forward in the development of a predictive understanding of the complex behavior of heterogeneous catalysts. So what has changed that leads us to believe that there are new scientific opportunities in this field? Why now? The key barriers to developing this understanding are the need to develop detailed knowledge of the *local* structure of the catalytically active site [the constituents at the active site(s) and their spatial arrangement at the atomic and molecular levels], the manner in which substrates and products interact with the active site, the temporal nature (activation, deactivation, and poisoning) of these interactions, and a detailed description of the overall reaction pathway(s). Detailed *local* structural information through an integrated approach would provide the necessary input to modeling and simulation tools that even at present can provide a good deal of insight where experiments are as yet unable to yield information directly. The development of new and emerging approaches to local structure determination have profited from the excitement for nanoscience and properties related to nanoscale entities over the last several years. Improvements in a variety of techniques and development of wholly new approaches to the study of materials properties have spawned emerging capabilities in structure determination of highly disordered or differently ordered systems, where the length scales of the important interactions are on the order of nanometers (the same length scale that has always been central to heterogeneous catalysis). Improvements in synchrotron X-ray sources and techniques;

local structure by neutron scattering brought about by brighter sources; new and vastly improved surface science techniques, such as scanning tunneling microscopy (STM); new solid-state NMR approaches to measure interatomic distances or temporal phenomena; and ever-improving computational capabilities that have enabled new simulation and modeling techniques are all poised to yield integrated new capabilities that can be brought to bear on complex, catalyst systems that to date have defied structural definition.

Because catalyst materials and processes are so complex, breakthroughs in catalysis will follow from an integrated approach. These breakthroughs will support development of efficient processes that generate, store, and utilize fuels for our future energy security. No single technique is capable of this task, and multiple particle-, photon-, or neutron-based, and advanced spectroscopic techniques must be brought to bear simultaneously on a catalyst system. Data from these disparate techniques and the observed reaction chemistry must be analyzed in a coherent fashion to yield a self-consistent depiction of the catalyst structure and dynamics. This will require new computational techniques with greater accuracy to allow for the integration with high fidelity of data from the various techniques. Improved and new theoretical approaches must be developed to allow for the interpretation, interpolation, and extrapolation of structure and properties when experimental techniques cannot access the needed data directly.

In the future, it is anticipated that new scientific developments, both experimental and theoretical, that allow for detailed descriptions of catalyst structure and dynamics under reaction conditions will have an impact on all aspects of catalysis research. In the transportation sector, the predictive capability generated by detailed structural information of reacting heterogeneous catalysts will have an impact on future developments in fuels synthesis (hydrogen, biofuels, etc.), energy storage (hydrogen, batteries), and fuels utilization (fuel cells) and will continue to play an important role in the mitigation of the environmental impacts of energy production and fuel utilization. The role of new experimental and theoretical approaches to defining the structure and properties of heterogeneous catalyst systems will have an impact on the fields of electrocatalysis and photocatalysis.

Major science needs for the future include:

- Further development of emerging and discovery of wholly new local structural tools that can probe the length scale of 0.1 to 2 nm.
- Developments that will allow the application of the techniques under realistic (in situ) catalytic reaction conditions, as well as applying multitechnique approaches for studies of active catalysts.
- Catalysis-related infrastructure (sample activation, *in-situ* reactivity studies, etc.) at DOE User Facilities, including catalysis end stations at beam lines and flight paths at X-ray and neutron sources and *in-situ* reactors for state-of-the-art surface science and NMR facilities.
- Computational models of the governing catalytic reactions and approaches to integration of structural and spectroscopic data from the above to yield self-consistent models of catalyst active sites, gas conversion and particulate oxidation.
- New nanoscale synthetic approaches that will allow generation of model active sites identified from knowledge achieved in the above pursuits.

Relevance and Potential Impact

Research will enable a considerably more secure energy future by providing fuel and fuel utilization options through more atom- and energy-efficient new catalysts and catalytic processes. It will have relevance to several applied DOE programs including the FreedomCar and Hydrogen Programs, Alternative Feedstocks for Fuels/Biofuels Programs, and Industrial Technologies Programs under EE/RE: Coal and Natural Gas Conversion Programs, Electric Power and Fuels R&D Programs (FE); and Science and Technology Programs (EM).

Estimated Time Scale

It will take approximately a decade to establish capability to fill the knowledge gaps.

THERMOELECTRIC MATERIALS AND ENERGY CONVERSION CYCLES FOR MOBILE APPLICATIONS

EXECUTIVE SUMMARY

Thermoelectric materials, in which heat can be transformed directly into electrical energy and that can act as solid-state heat pumps, have begun to be used in transportation systems. As such they have the capability to mitigate the energy loss in transportation systems associated with heat loss. At present, theoretical considerations suggest that automotive efficiencies could be increased by 20% simply by capturing the waste heat, an efficiency gain comparable to what would be obtained by converting the U.S. car and light-truck fleet to diesel engines, but without the penalty in NO_x or particulate emissions. In addition, thermoelectric materials will lead to an all solid-state, reversible automotive air conditioning system that does not use greenhouse gases and can be simpler and more efficient to operate. Realizing such gains depends on finding materials which behavior meets theoretical limits. These theoretical limits are rooted in the transport properties of materials, which in turn depend on their nanostructure and composition. For example, quantum wires and dots embedded in a suitable matrix appear to have greater potential for use in thermoelectric devices than alloys or other homogeneous materials. Prototypical systems built to demonstrate the above gains are likely to be realized in practice, again depending on the discovery of appropriate materials and the means for fabricating them. Recent new heat exchange cycles between the thermoelectric elements and the working fluids (i.e., exhaust gas, passenger compartment air, or liquids) have also been proposed that make optimal use of each thermoelectric element in a thermoelectric pile and can potentially lead to a substantial increase in system efficiencies.

Summary of Research Direction

A combination of environmental, economic, and technological drivers has led to a reassessment of the potential for using thermoelectric (TE) devices in several transportation applications. In order for this technology to achieve its ultimate potential, new materials with enhanced thermoelectric properties are required. Also, as each TE element is small, unconventional thinking in the area of new heat exchangers between the TE elements and the working fluids will lead to new TE energy generating and cooling systems. These will lead to further increases in efficiencies.

Thermoelectric materials convert heat into electrical energy with an efficiency that is a function of a material parameter defined as the thermoelectric figure of merit, Z . When used as solid state heat pumps in cooling systems, the coefficient of performance of the system (COP), defined as the ratio of the heat extracted at the cold side to the total energy consumed, is again a function of the same figure of merit Z . It is usual to express Z in dimensionless units by multiplying it with the average operating temperature, T . Commercially available thermoelectric materials have a dimensionless figure of merit, $ZT = \sim 0.9$ near room temperature. For a temperature difference of 40°C , typical of an automotive air conditioning system, the COP is on the order of 0.25.

Recent engineering developments with cross-flow heat exchangers that make optimal use of the thermoelectric elements within the cooling modules more than double the COP that can be obtained with a material of a given ZT , and similarly could double the efficiency of TE generators. Even with this, the efficiencies and COP's that can be reached with commercial TE materials are still insufficient. Recently nanoscale thermoelectric materials have been demonstrated that have $ZT=2$. With such materials, refrig-

erator systems can be calculated to reach COPs competitive with vapor compression. Waste-heat recovery systems could theoretically reach 13% efficiency, potentially improving the mileage of vehicles by over 20%.

The above improvements in ZT are a direct result of recent progress in the understanding of electronic and thermal transport properties in two areas of solid-state physics: (1) semiconductor quantum wells, wires and dots, and (2) crystalline solids with low thermal conductivities. These transport theories may need further development, but they point to the possibility of further increasing ZT to 4 or even 6, resulting in COPs close to double that of vapor compression air-conditioning and waste heat recovery. This could result potentially in a theoretical increase in fuel economy perhaps larger than could be expected from increasing the use of diesel fuel systems in the U.S. fleet.

New Scientific Opportunities

Scientific research on new material systems which properties approach the theoretically predicted improvements should include nanocomposites and crystals with glass-like thermal conductivity. New concepts to synthesize the new materials in industrial quantities must be explored. New concepts for the optimal use of these materials in complete TE systems, in which segmentation of the thermocouples, the efficiency of the heat exchange with the working fluids, and the problems of making low-resistance contacts to the TE materials are paramount, will greatly improve the efficiency and the economics of heat recovery systems and air conditioners.

Relevance and Potential Impact

Heat recovery systems. In a gasoline engine, roughly two-thirds of the chemical energy of the fuel is wasted as heat, half in the engine coolant and half in the exhaust gas stream. An additional ~5% of the energy is wasted in friction losses and 2-10% goes to the alternator, leaving 15-35% of the fuel energy for propulsion. TE systems can directly and simply convert waste heat into electricity. There are two potential uses for this. In a conventional vehicle (see Figure 6-1), the TE generator can potentially unload the alternator, which (depending on the operating regime) utilizes 2-10% of the energy in the fuel. Assuming a reasonable system efficiency (i.e., 6-9%), a TE generator could supplant the alternator, producing a fuel economy improvement of 2% of the fuel energy or ~5-10 % in the vehicle's mileage.

In future vehicles with hybrid or electric propulsion (see Figure 6-2), the electrical energy saved can be used for propulsion. The efficiency of the TE generator now comes into play directly. With an ~10% conversion of waste heat to electricity, roughly 5% of the chemical energy of the fuel can be recovered. Assuming that, on average, only about 25% goes to propulsion overall, this represents a potential 5%/25% or ~20% improvement in fuel economy. Such benefits are comparable to those obtained by using diesel engines rather than gasoline engines, but without the environmental issues (i.e., NO_x and particulate emissions) associated with diesel technology.

Transportation R&D is a major component of the DOE's EE/RE program.

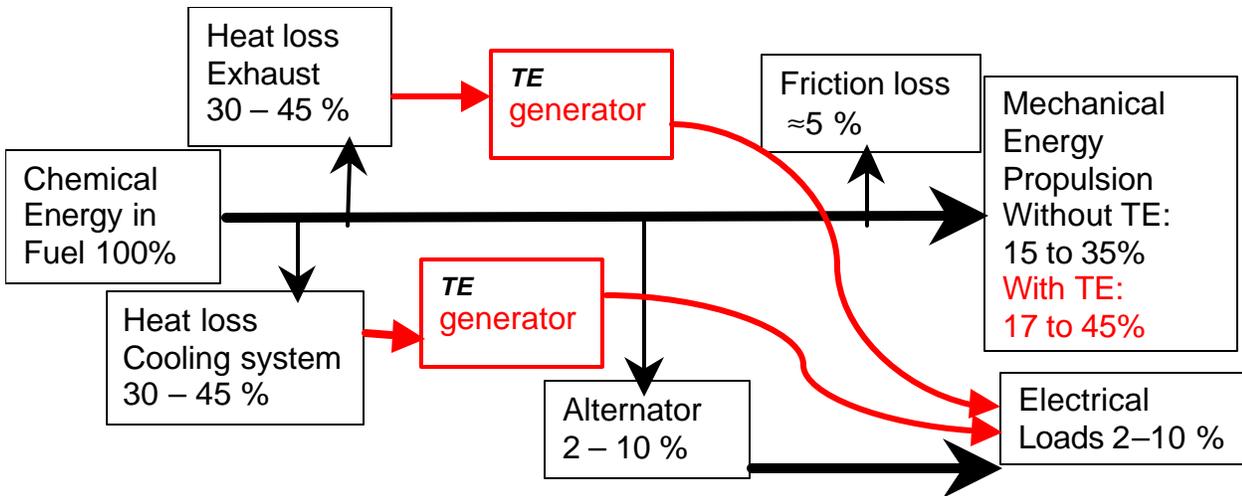


Figure 6-1. Energy use in a conventional vehicle (black lines). A thermoelectric generator (red line) can unload the alternator, leading to a fuel economy improvement of 4-10%.

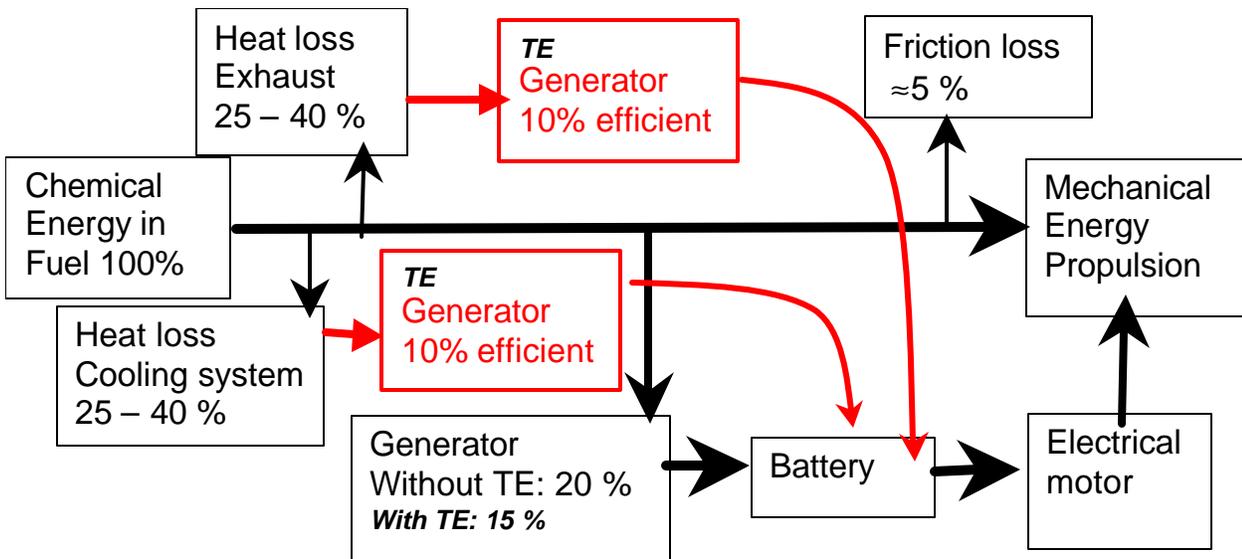


Figure 6-2. Energy use in a vehicle in which supplemental electrical propulsion is available (black lines). A thermoelectric generator (red line) can supplement the electrical generator, leading to a fuel economy improvement of up to 20%.

Climate Control. Thermoelectric climate control in automotive systems is attractive from the point of view of simplicity and environmental friendliness. In 1974 it was first suggested that chlorofluorocarbon compounds, principally R12, or freon (the refrigerant of choice in air conditioning systems for the last 50 years), were destroying the protective ozone layer in the stratosphere at an alarming rate. As a result, the Montreal protocol of 1987 has led to a gradual phasing out of these harmful chemicals. In their stead, non-chlorine-containing fluorocarbons, such as R134a, which do not possess the long-term stability of R12, have widespread use as refrigerants. It was not realized until quite recently, however, that all fluorocarbons, including R134a, can contribute to global warming. This is because these gases are capable of absorbing the infrared radiation the earth emits to stabilize its temperature. The infrared-absorbing capability of a gas is measured by its Global Warming Potential (GWP) index. The GWP index measures the absorption characteristics relative to that of CO₂, which is defined to have a GWP index of unity. The GWP indices of R12 and R134a are 8,500 and 1,300, respectively. In other words, 1 kg of R12 and R134a are equivalent to 8,500 and 1,300 kg of CO₂, respectively, in terms of their global warming impact. Thus even relatively small amounts of these chemicals released into the atmosphere (e.g., via leakage) can have serious consequences in the long term. In light of these sobering facts, it is natural to contemplate alternative cooling technologies, which might supplant vapor compression systems containing such chemicals. Thermoelectric cooling is one such alternative that presents many advantages, including all solid-state operation, electronic capacity control, reversibility to provide both heating and cooling, and high reliability. In spite of these many benefits, thermoelectric cooling has not enjoyed widespread or large-scale use due to the low efficiency relative to vapor compression systems [D. T. Morelli, *Proc. Mat. Res. Soc.* **478** 297, 1997, with permission].

Refrigeration is relevant to transportation as well as a number of other industries. Within DOE, the applied research in these areas is part of the EE/RE Program.

Estimated Time Scale

Applications in high-end industries are possible within the next 10 years. However, broader uses will require more significant advancements with a likely 20-year research horizon.

COMPLEX SYSTEMS SCIENCE FOR SUSTAINABLE TRANSPORTATION

EXECUTIVE SUMMARY

The transportation sector poses particularly formidable challenges from the perspectives of energy security and sustainability because of its strong reliance on petroleum-based fuels and the complexity of the overall transportation system. The emerging science of complex systems offers exciting possibilities for providing new insights and research tools to address these challenges in a broad multidisciplinary manner that balances the collective needs of society with those of individual stakeholders. With its emphasis on nonlinear, holistic, and dynamic behaviors and on organic, evolutionary models that highlight such issues as contingency, self-organization, adaptation, and robustness, the complex systems approach naturally incorporates many of the concepts that need to inform rational decision making on pathways to more energy-efficient and sustainable transportation (i.e., that meets future demands for mobility with minimal unintended ecological and socioeconomic consequences). Long-term basic research in this area is needed to develop the fundamental concepts, tools, and cross-disciplinary insights that will help to clarify the scientific criteria for sustainable transportation and effective strategies for addressing the multitude of challenges that may require more than purely technological advances. Shorter-term activities need to focus on accelerating the practical impact of more established complex systems tools (e.g., nonlinear systems dynamics, logistical optimization, agent-based modeling, network theory and game theory) and gaining experience in addressing complex transportation issues. One example of the type of important, but nontraditional, problem this approach may begin to address immediately is the planning of an efficient and robust strategy for transporting nuclear waste from distributed sources to the Yucca Mountain disposal site.

Summary of the Proposed Research

The Challenge of Sustainable Transportation. Modern transportation systems have given the industrialized world an unprecedented degree of mobility, which has been instrumental in improving the quality of life, fostering democratic values, and promoting economic prosperity. Ensuring the sustainability of these systems for the foreseeable future is a particularly formidable challenge. From a technological perspective, petroleum-based fuels are nearly ideally suited as a mobile energy carrier. Energy security concerns, however, (especially an increasing U.S. reliance on foreign oil and growing evidence for global climate implications of CO₂ emissions) have greatly accelerated the search for alternative decarbonized fuels and more efficient powertrain technologies. Furthermore, the transportation sector is increasingly challenged by a large number of other unintended environmental and socioeconomic consequences, such as air quality concerns, ozone depletion, landfill utilization, sprawl, congestion, noise, and vehicle-related fatalities and injuries, the costs of which are nearly all “externalized” to society at large.

Today’s global transportation “system” includes many different modes of transportation and their associated fuels, vehicles, infrastructure, policy issues, market pressures, and the needs, expectations and behaviors of end users. While impressive progress has often been made in dealing with various components and issues individually, that approach generally leads to suboptimal collective behavior and may be reaching a point of diminishing returns in terms of purely technological solutions to long-standing problems (e.g., close to 99% reductions in tailpipe CO, hydrocarbon, and NO_x emissions).

By themselves, traditional scientific disciplines and lines of inquiry are ill suited to address the full scope of the complex interdependencies and multiple time scales required to provide future generations with the same access to and benefits of mobility as we enjoy today, without undue economic, ecological, or sociological hardships. Intra-generational equity between the developed and developing world is also a critical and contentious issue, given that transportation represents the most rapidly growing sector in terms of energy demand, with most anticipated growth in currently undeveloped regions.

Opportunity for Complex Systems Science. There is clearly a need for a more integrated, multidisciplinary, scientific approach and new fundamental insights to help guide the development of and transition to more sustainable transportation systems. An exciting and promising research area in harmony with this challenge is the emerging science of complex systems. This field seeks novel regularities that cut across all fields of human knowledge and a balance between the prevailing scientific and industrial world view (with its emphasis on linearity, reductionism, and equilibrium) and a more nonlinear, holistic, and nonequilibrium perspective. Through mathematical models and computer simulations, complex systems research offers the potential to move away from mechanical analogies and their focus on predictability and optimization to more organic, evolutionary models that highlight such issues as contingency, diversity, robustness, and adaptation. The latter themes offer exciting opportunities to exploit biological insights into sustainability as a bridge between the physical and social sciences and to improve strategic decision making in the face of uncertainties associated with a coevolving environment, network effects, coupled time and length scales, and strong path dependencies.

Among the key questions pertaining to sustainable transportation that complex systems science can potentially address are:

- How do economic, cultural, institutional, and technological factors interact to shape transport patterns and their associated environmental and socioeconomic impacts?
- How do varied modalities of mobility (e.g., road vs. air, people vs. freight) complement and conflict with each other, and how do individual agents devise strategies and make choices as a result?
- What are the leverage points conducive to interventions toward more sustainable transportation systems and effective strategies for overcoming irrational systems archetypes (e.g., tragedy of the commons, shifting the burden) that might inhibit progress?

The degree to which answers to such questions may be reasonably independent of scale is itself an exciting opportunity for research. Lessons learned in local communities, for example, may translate into effective strategies at national and global levels. Smaller-scale problems also lend themselves to experimentation and to detailed investigation of the links between individual agent behaviors and the collective properties of the system. The complexity of the sustainable mobility challenge implies that there are unlikely to be any magic bullets, and that even the goal of seeking optimal solutions may be misguided. Instead, what research in this area promises is a process for creating a systematic approach to all relevant knowledge and for improving our ability to anticipate and avoid or mitigate non-intuitive unintended consequences of proposed actions.

New Scientific Opportunities

The proposed work divides naturally into two time-frames:

- **Longer-Term Fundamental Research.** The science of complex systems is largely in its infancy. Developing the requisite concepts, tools, and cross-disciplinary insights to address the multitude of sustainability challenges will clearly be an ongoing process, especially in light of still-to-be discovered environmental and socioeconomic concerns and technological options. Creative work of all kinds in this area needs to be encouraged.
- **Shorter-Term Applications.** In parallel with an ambitious long-term program, it would be beneficial to initiate shorter-term research to accelerate the practical impact of existing complex systems methodologies and to explore their implications for specific sustainable transportation challenges. Among the most fertile areas of current complex systems research are network theory (structure and dynamics), game theoretical studies of social behaviors (e.g., the evolution of cooperation), agent-based modeling, time-series analysis, evolutionary algorithms, and informatics and nonlinear dynamics in general. Traffic modeling as a nonlinear flow problem is already an active area of research that deserves further attention in all aspects from fundamental concepts to practical infrastructure planning and real-time traffic routing tools. A combination of existing tools might be useful for providing integrated assessments of technological and socioeconomic issues in the context of evaluating the practicality and robustness of proposed pathways to major infrastructure changes (e.g., from petroleum to hydrogen). Another application that needs immediate attention from an energy security perspective is the development of an efficient, safe, and socially-acceptable strategy for transporting nuclear waste from distributed sources to the Yucca Mountain disposal site.

Relevance and Potential Impact

This PRD is truly out-of-the-box and addresses some of the most critical, but most easily ignored, issues that inhibit progress in all DOE energy programs. The main themes here, of recognizing the systemic nature of problems and the desirability of considering environmental and socioeconomic aspects on the same footing as technological, are particularly relevant to the transportation sector. However, the insights and methodologies developed will also apply to problems in distributed energy, the diversity of renewable energy options, nuclear fuel systems, etc. The work proposed is high risk in the sense that complex systems science is still in its infancy and its practical impact is largely unproven. However, the potential societal benefits are enormous, and the research is sure to foster a great deal of exciting and important progress that will complement and leverage existing DOE initiatives at the scientific frontier of complexity.

Estimated Time Scale

It is understood that this type of research is not currently supportable by DOE.

Residential, Commercial, and Industrial Energy Consumption

Sensors

Solid State Lighting

Innovative Materials for New Energy Technologies

Multilayer Thin Film Materials and Deposition Processes

SENSORS

EXECUTIVE SUMMARY

Optimizing energy performance in residential and commercial buildings will require a new generation of smart controls whose function is driven by a new generation of sensors. Similarly, the application of smart sensors that monitor, control, and optimize production and manufacturing processes will also lead to efficient energy use in large-scale industrial processes. In many small-scale applications (e.g., appliances), sensors must be highly specific to an environmental parameter, robust, rugged, durable and low cost. In larger-scale building and industrial processes and applications, there is also the demand for a ubiquitous network of small, wireless, self-powered sensors with associated on-board signal processing, networking, and communications capabilities.

Summary of Research Direction

Residential and Commercial Buildings: The operation of the current generation of buildings is characterized by a small number of simple sensors with fixed response modes. A room thermostat with a temperature sensor and simple feedback loop is a well-known example. In order to achieve significant breakthroughs in building energy efficiency, buildings must become dramatically more intelligent, self-aware, and dynamic in response to weather changes, energy use and changing occupant needs. Buildings should have the ability to sense and then control energy flows, temperatures, airflow, pollutant levels, and other specific physical parameters, both within the building structure and in its component elements and equipment.

A prototypical smart system will include four generic elements:

- self powered sensors,
- signal processing,
- wireless communication between sensors and to control systems, and
- intelligent response based on a sensed event.

Industrial Sectors: Manufacturers today must continuously improve process operations, product quality, and productivity with fewer workers than ever before. Processing equipment must deliver unprecedented levels of reliability, availability, and maintainability as plant managers seek to reduce operational and support costs and minimize capital investments.

Advanced and wireless sensor systems will enable manufacturers to meet the demands of increased competitiveness by helping them to streamline process operations and to use energy and materials more efficiently. As in the case of buildings, industrial sensors should provide real-time, continuously sensitive monitoring of a specific function and provide diagnostics to continuously maintain the functionality and energy efficiency of operations. Sensor systems in industrial applications, however, face unique challenges: invulnerability to harsh environments and high reliability. Sensor systems must reliably perform mission-critical tasks over extended, pre-defined periods in environments characterized by

- extremely high (up to 2,600° F/1,430° C) and low operating temperatures,
- strong vibrations,

- airborne contaminants,
- excessive electromagnetic noise caused by large motors or conductors,
- exposure to harsh, corrosive chemicals,
- high humidity levels,
- potentially explosive situations, and
- mobile and stationary metal equipment affecting transmission pathways.

New Scientific Opportunities

Residential and Commercial Buildings. Two areas of scientific breakthroughs are needed to achieve the aforementioned vision.

The first needed breakthrough is a new generation of smart sensors that can detect and measure a wide range of physical and chemical parameters. The sensors should be small, self-powered, low cost, durable, and robust in order to work under a wide range of physical environments, with detection capabilities that are specific to the parameter of interest, such as chemical species, particle size and/or shape, etc. Very low cost sensors allow redundancy that will improve accuracy. Sensors would be available to respond to a full range of stimuli, such as optical and radiant measurements, surface acoustic waves, airflow, chemical species, biological agents, inorganic particles, energy flows, magnetic fields, current, voltage, temperature, stresses, etc. On board, integrated electronics provide signal processing, conditioning and data compression, if needed.

The second needed breakthrough is an information technology infrastructure that allows data from sensors to be collected, processed, and converted into useful information upon which action can be taken, thereby reducing energy use or providing other useful functionality. The same need is reflected in the industrial sector. The new paradigm is a dense network of ubiquitous, wireless, self-powered sensors that can be networked to provide a complete and reliable picture of energy use and related parameters throughout a building and its equipment. Wireless communications protocols that are energy efficient will allow very long battery life or will support stand-alone operation using scavenged energy. Open protocols that are standardized across many business sectors will ensure interoperability of sensor and network components. Neural networks and adaptive logic can be utilized to adjust and fine tune the operation of the building to meet changing occupant needs and external events, such as real time utility pricing.

Industrial Sector. Advanced industrial materials and control are needed to meet the challenges to sensor placement in the industrial sector. A list of proposed research directions is provided below:

- **Improved Controls/Process Modeling** – A process control system or algorithm that increases process stability, optimizes operations, or improves product quality. The system should use adaptive control, neural networks, or other advanced control technology. Development of the control system may require improved modeling or process simulation tools.
- **Chemical Composition** – Better understanding of spectroscopic techniques; more reliable and cheaper laser techniques to measure chemical composition; better understanding of chemo-metrics; ability to do chemical analysis of nanoscale samples.
- **Physical Properties** – Real-time sensors or techniques to measure a specific process condition(s), such as temperature, pressure, flow, web tension, or multiphase flow.

- **Signal/Numerical Processing** – Improved signal processing, especially for the purpose of predicting fouling, detecting equipment faults/failure, predicting process upsets, or correcting sensor drift. The signal processing algorithm should be used to process raw sensor data output into usable process information. This can be in the form of a “smart sensor” that detects failure or drift, and then self-calibrates.
- **Imaging/Machine Vision** – Real-time sensor or measurement technique for visual inspection of product, specifically looking for defects, inclusions, color, and cleanliness, as well as measuring product properties for quality.
- **Emissions Measurement and Control** – Measurement and control techniques for combustion emission control applications.

Relevance and Potential Impact

The potential impacts of smart sensors on energy savings in the residential, commercial, and industrial sectors are achievable on many different scales, ranging from single appliances, complete building systems, to large-scale industrial processes. They share the common objective of providing an “information rich environment” in which intelligent decision-making will greatly enhance energy efficiency, occupant health, comfort and operating efficiency.

Single building appliance. At the level of a single energy-consuming device, there are important energy savings to be achieved. For example, dishwashers typically employ a series of wash cycles based on the assumption that dishes will be dirty, even though many people prewash dishes. Energy consumption for hot water and energy to drive the dishwasher is based on this assumption. New machines use a novel optical sensor that directly monitors the turbidity of the wash water as a metric for cleanliness. Coupled with adaptive logic controls, the dishwasher provides clean dishes with less water and lower energy use. Sensors for consumer product applications must be robust, reliable and low cost, thus challenging designers to employ new technologies that meet performance needs.

Building systems. A broader vision of energy-efficient buildings assumes that buildings can be optimally operated as a wholistic mechanism that is more than the sum of its parts. Real-time, continuous monitoring and diagnostics allow the building to continuously maintain operations in a mode that provides the required functionality and energy efficiency, as well as meeting human comfort and health needs. In the event of unanticipated disturbances, either natural or man-made, the building can adapt and respond in a manner that enhances safety and security. Continuous monitoring allows routine and preventive maintenance to be cost-effectively scheduled.

Industrial processes. Many of our most energy-intensive industries have identified and highlighted their top needs in the development of sensor, control, and automation systems. Highest priority is placed on systems that can truly revolutionize manufacturing processes as, for example, by enabling replacement of a batch process with a continuous one. Such advances will result in major reductions in manufacturing cost and energy consumption. In addition, wireless industrial sensor systems offer manufacturers greater mobility and flexibility. Freed from the constraint of wires, plant managers can more easily track materials flow and reconfigure assembly lines in response to demand. An effective wireless sensor technology is envisioned as robust, reliable, cost-efficient, totally secure, and in many cases, integral to the measurement device.

Estimated Time Scale

The development and integration of wireless sensor networks could benefit from the advances in the semiconductor industries and could have some success in the next 1-3 years time frame. For all sectors, advanced materials research to enable smart materials design is a rather long-term goal with a development period of ~5-10 years needed. The length can be shortened by an aggressive program to ~3-5 years. To enable the discovery of new classes of materials for sensors with revolutionary selectivity, sensitivity, reliability, and durability in harsh environments, 10-15 years may be required.

SOLID STATE LIGHTING

EXECUTIVE SUMMARY

This year, about 20% of the U.S.'s electricity consumption will be due to lighting. Incandescent and fluorescent bulbs, old vacuum-tube-based technologies that have been around for decades, will provide the vast majority of that lighting. Incandescent light is quite inefficient, with only 5-6% of their electricity consumption being converted to visible light. The rest is converted to waste heat, which contributes significantly to building cooling loads. Fluorescent lighting is better, but still only converts about 25% of the electrical energy into visible light. This wasted electricity represents an enormous target for reducing energy consumption.

Solid-state lighting (i.e., the use of light-emitting diodes, or LEDs, for general illumination) is a new technology that has the potential to far exceed these energy efficiencies. Within the past few years, two innovative new semiconductor materials – wide bandgap semiconductors and organic light emitting materials – have enabled the development of the first LEDs with bright emission in the blue and near-ultraviolet (UV). With these colors, white LED light sources can now be realized based on the color mixing of different wavelength light from multiple LEDs, or the down conversion of UV or blue light to longer wavelengths (green, red) using phosphors. While tremendous progress has been made in the last decade – today's white LEDs are more efficient (25 lumens/Watt) than incandescent bulbs (15 lumens/Watt) – there is much fundamental materials science that must be done for further progress to be made. Ultimately, it should be possible to reach the stretch goal of 200 lumens/Watt in the next 1-2 decades, with an LED cost that is competitive with incandescent and fluorescent bulbs. The achievement of this goal would result in spectacular energy savings, a 50% reduction in electricity used for lighting and a 10% reduction in total electricity consumption. Globally, this corresponds to an 1100 billion kWh/year reduction in power consumption, worth \$100 billion in reduced rate charges, and corresponding to reduced carbon emissions of roughly 200 Mtons/yr.

This proposed research direction seeks to increase fundamental understanding of basic physics issues, still poorly understood, in these relatively new solid-state lighting materials. Issues include charge transport, radiative and non-radiative electron-hole recombination, defect and impurity physics, growth chemistry and materials preparation physics, and aging and breakdown mechanisms. Three classes of materials are considered: (1) wide bandgap semiconductors (primarily nitride-based) for inorganic LEDs; (2) polymer-based materials for organic LEDs; and (3) new energy conversion and packaging materials to act as highly efficient phosphors and UV-stable, moisture-impermeable coatings for the LEDs.

Summary of Research Direction

At present, electricity is responsible for about 25% of the nation's total energy consumption. Of that, about 20% is due to lighting. Thus lighting represents a significant portion of energy consumption. However, conventional lighting technology, consisting primarily of incandescent bulbs and fluorescent tubes, is remarkably inefficient. Incandescent bulbs, which represent the major residential lighting source, convert only about 5-6% of their power consumption into visible light. Fluorescent lighting, which dominates industrial and commercial areas, is considerably better, with 25% energy efficiency, but nonetheless wastes a significant amount of energy as heat.

Recently, the development of new materials, both inorganic and organic, have enabled the production of white light using solid state technologies [i.e., light-emitting diodes (LEDs) and organic LEDs or OLEDs].

These new semiconductor-based lighting technologies promise to be more flexible, compact, robust, and longer lived than vacuum-tube-based technologies. LEDs and OLEDs offer the possibility of exceptional control over color, hue, and intensity, and can even be modulated at high rates, offering the possibility of simultaneous use for communications. But most importantly, LEDs and OLEDs offer opportunities for energy savings that are truly enormous.

Based on proof-of-principle demonstrations of lasers and LEDs in the red and infrared, it is believed that white LEDs operating at 50% efficiency might ultimately be produced. This corresponds roughly to an efficacy of 200 lumens/Watt. (By comparison, incandescent and fluorescent bulbs are typically 15 lumens/Watt and 80 lumens/Watt, respectively.) Achieving the 200 lumens/Watt goal would have an immense impact on electricity consumption. It would decrease by 50% the amount of electricity used for lighting, and decrease by 10% the total consumption of electricity. The reduction in the U.S. alone would be equivalent to all the electricity consumed by residential homes in the states of California, Oregon, and Washington. Global reductions of power consumption would be about 1100 billion kWh/yr, or about \$100 billion/yr in rate charges. This corresponds to a reduction of about 200 million tons of carbon emissions per year.

The materials physics advances that have enabled the realization of white LEDs and OLEDs are different for the two technologies. For LEDs based on inorganic compound semiconductor materials, the enabling material is GaN and other related nitride-based III-V compounds including InN, AlN, and their ternary and quaternary alloys. This class of materials is generally referred to as wide bandgap semiconductor compounds. For organic LEDs, the enabling materials include Alq3 (a flexible, light emitting polymer), polyfluorene, and related polymers and small molecule organic materials. In both cases, the materials have become available only within the last ten years, and much of their fundamental physics is poorly understood at present. Progress has been rapid over the past decade, with inorganic white LEDs now producing 25 lumens/Watt, and organic OLEDs producing 6 lumens/Watt. However, much of this recent progress has been due to relatively uninformed phenomenological explorations of parameter space, and it is widely acknowledged that without detailed scientific understanding of these materials, further progress will be more difficult. Basic investigations of the physics of how these materials are synthesized, how electron transport occurs through them, how dislocations and other defects affect their properties, and fundamental questions about band structure, impurity levels, electron-impurity interactions, physics and chemistry of electrical contact formation, radiative and nonradiative electron-hole recombination mechanisms, spontaneously formed micro- and nanostructures, and degradation mechanisms at high current drive levels, are needed. With detailed knowledge of the fundamental science underlying these processes, it is expected that we will be able to specifically tailor the properties of these materials, so as to raise the overall efficiency with which they produce visible light, increase LED and OLED lifetime and reliability, and lower the cost by orders of magnitude.

New Scientific Opportunities

In order to achieve the 200 lumens/Watt goal for the LED/OLED devices, the following is a list of proposed scientific opportunities which are broken into three categories. These are (1) inorganic wide bandgap semiconductor LED materials, (2) organic OLED materials, and (3) energy conversion materials and associated UV-stable packaging materials.

Inorganic Wide Bandgap Semiconductor Materials. The nitride-based III-V compounds have a number of properties not seen in other III-V semiconductors. These include the lack of a native lattice-matched substrate (the large stresses that develop in heterostructures due to lattice mismatches between AlN, GaN, and InN) lack of a shallow level acceptor impurity for p-type doping; and poorly understood and poorly controlled chemical vapor deposition growth processes. In this area we propose research on:

- Innovative growth methods for reducing defects and tailoring residual stresses via innovative synthesis processes, as well as developing large area (diameter >2") lattice-matching substrates.
- Microscopic understanding of the role of doping, impurities, and their interactions with structural defects. Specifically, approaches to higher p-type doping levels, particularly for higher Al compositions.
- Investigations of fundamental processes involved in the chemical-vapor-deposition growth of nitride materials. Novel growth reactor designs with improved repeatability, temperature control, in-situ growth monitors, and more efficient use of precursor gases should proceed with further understanding of growth chemistry.
- Novel light emitting device designs to reduce parasitic resistances, increase internal quantum efficiency, and increase light extraction efficiency with the aim of tailoring the direction and amplitude of the photonic density of states.

Organics. Organic light-emitting diodes (OLEDs), although still in their infancy, hold tremendous promise as an energy saving light source, but continue to face deep and broad technical challenges. Performance limitations can be partly attributed to the very low carrier mobilities in these materials. At present, green OLEDs with efficiencies of 60 lumens/Watt have been demonstrated, but OLED lifetimes are observed to drop dramatically as drive current densities are increased to the levels needed for general illumination. Questions to be answered include:

- What is the chemical and electronic structure of the material interfaces?
- Why are luminescent efficiencies so high in some organic materials as opposed to others?
- What controls the singlet-triplet exciton formation ratio in conjugated materials?
- Why do shorter wavelength (blue, violet) devices tend to have lower luminous efficacy?
- Is it possible to modify materials to increase their stability in humid environments?
- What are the intrinsic mechanisms that lead to material degradation? How and why do these mechanisms depend on drive current?
- What is the chemical and electrical structure of the electrical contacts? What modifications can increase performance?

Energy conversion materials and UV-stable packaging. Phosphors are currently in use in fluorescent lamps, and a number of high-efficiency phosphors which can yield high-quality, high color rendering index (CRI) white light have been developed for fluorescents over the past several decades. However, the current fluorescent phosphors were optimized for the wavelength of the mercury vapor discharge in fluorescents, and are unsuitable for the >380 nm pump wavelength appropriate for white LEDs. In addition to new "conventional" phosphor materials, a number of other more novel approaches are possible. This

topic considers basic physics investigations of a number of different materials approaches to energy conversion for solid state lighting, and the associated packaging material in which the phosphors will be distributed. Research is proposed on:

- Nanocrystalline quantum dots (CdSe, ZnS, etc.) for use as “phosphors,” whereby the optoelectronic properties are controlled by quantum dot size and surface treatments.
- Novel inorganic semiconductor structures incorporating one or more near-surface quantum wells that act as phosphors, absorbing light from the nearby active region and re-emitting at a longer wavelength.
- “Nanophosphors,” in which “conventional” phosphor material is produced on the particle size scale of a few tens of nanometers, eliminating backscattering of light into the LED and enabling highly efficient particle packing.
- Novel encapsulant materials that will withstand high flux UV irradiation and elevated temperature, block out moisture, and have small thermal expansion coefficients.

Relevance and Potential Impact

This PRD will be relevant to the programs at EE on (1) wide bandgap materials for photovoltaic power conversion and control, (2) wide bandgap materials for sensing and logic in high temperature, high pressure environments (e.g., down-hole sensing in oil wells), and (3) new polymers and other organic materials for cheap, large-area solar cells. The PRD will also serve the non-energy related DOE needs in the following aspects: (1) wide bandgap materials for high power electronics for synthetic aperture radar, and ultra-light imaging radar systems for Unmanned Aerial Vehicles (UAV), (2) solar blind UV-photodetectors, for detecting missile launch plumes, and (3) low power, compact UV sources for UV-fluorescence-based detection of chemical, biological, and nuclear weapons of mass destruction. A particularly appealing application is compact portable anthrax detectors.

Estimated Time Scale

More in-depth understanding on the device physics and degradation mechanisms in LED and OLED devices could be achieved in 10 years. It will require up to 20 years to integrate these findings into reaching the stretched performance goals of 200 lumens/Watt of LED/OLED devices that are cost competitive with incandescent and fluorescent light sources.

INNOVATIVE MATERIALS FOR NEW ENERGY TECHNOLOGIES

EXECUTIVE SUMMARY

The last decade has seen major advances in the fields of nanoscience and nanotechnology, advances that now enable scientists to control the chemistry and arrangement of matter at length scales 100,000 times smaller than the width of a human hair. Because of the fact that elementary energetic processes naturally occur at these same ultra-small length scales, these advances offer unprecedented opportunities to dramatically change the way we store, convert and use energy. Taking nature's construction of cells and tissues as our inspiration, it is now possible to imagine building, from the "bottom up," complex, hierarchical molecular organizations whose properties and functions reach far beyond those exhibited by their organic and inorganic building block components. The aim of this proposed research direction is thus towards the development of innovative materials for new energy-related technologies.

In the area of energy conversion, nanocomposite polymer/semiconductor assemblies are sought for next generation high-efficiency (~30%), low-cost solar cells for commercial and residential use in sunny geographical locales, as well as new thermoelectric materials for the conversion of waste heat to electricity and novel membranes and catalysts for stationary fuel cells. The transition to clean, renewable energy sources for mainstream commercial, residential and transportation applications further hinge upon substantial innovations in energy storage. The high interface per volume intrinsic to nanocomposite materials could open the path to a long-sought high-power, high-energy density, all solid-state rechargeable battery with performance, cost and ES&H (Environmental, Safety and Health) attributes that far surpass today's very best portable power storage devices. Looking even further into the future, chemical/molecular-based approaches that mimic the biological ATP-ADP engine would represent a revolutionary advance in energy storage. Finally, innovative materials can play a central role in reducing commercial and residential energy usage, which now accounts for ~37% of our total domestic energy consumption, through more efficient and durable building materials, and building elements that sense and respond to their environment. For example, replacement of today's less-efficient fluorescent and incandescent lighting with organic light-emitting devices would translate to a huge energy savings, with an associated reduction in carbon emissions from the energy points of origin, while "active" materials systems that could respond to climatic/lighting changes, such as phase-change building materials and smart electrochromic windows, could substantially reduce the energy spent on space heating and cooling (~35% of residential energy use).

Summary of Research Direction

The last decade has seen major advances in the fields of nanoscience and nanotechnology, advances that now enable scientists to control the chemistry and arrangement of matter at length scales 100,000 times smaller than the width of a human hair. These advances offer unprecedented opportunities to dramatically change the way we store, convert and use energy, because elementary and highly efficient energetic processes naturally occur at these same ultra-small length scales. Taking nature's construction of cells and tissues as our inspiration, it is now possible to imagine building, from the "bottom up," complex, hierarchical molecular organizations whose properties and functions reach far beyond those exhibited by their organic and inorganic building block components. The aim of this proposed research direction is thus towards the development of innovative materials for new energy-related technologies.

An example from energy conversion where nanostructured assemblies could favorably impact both energy security and the environment is in solar cell technology. Solar cells convert light to electricity by absorbing

light of sufficient energy to excite electrons across the bandgap and into the conduction band of a semiconducting material. While silicon-based solar cells have been under commercial development for decades, their widespread use has been precluded by cost and efficiency considerations. Solar cells based on new materials, such as nanocomposite arrays of colloidal semiconductor nanorods embedded in a conductive polymer, hold promise as an inexpensive route to high-efficiency (30%) energy conversion devices for commercial and residential use in sunny geographical regions. Other advanced energy conversion strategies for these sectors similarly hinge upon materials developments, including thermoelectrics for the conversion of waste heat to electricity and membranes and catalysts for stationary fuel cells.

Beyond energy conversion, great fundamental research challenges must be addressed in the energy storage arena, particularly if clean, renewable energy sources are ever to graduate into mainstream use in the commercial and residential sectors, as well as transportation. Here again, recent progress in controlling materials structure and properties at the nanometer level can play an enabling role. For instance, the high interface per volume intrinsic to templated, nanocomposite materials could open the path to a long-sought high-power, high energy density, all solid-state rechargeable battery with performance, cost and ES&H attributes that far surpass today's very best portable power storage devices. Looking even further into the future, chemical/molecular energy storage approaches that mimic the biological ATP-ADP engine could revolutionize the very way we harness and use energy to such an extent that the full implications of an advance of this nature are difficult to project.

Finally, innovative materials can play a central role in energy security by reducing our commercial and residential energy usage, which now accounts for ~37% of our total domestic energy consumption, through more efficient and durable building materials and building elements that sense and respond to their environment. An example is in the area of lighting, which represents ~20% of the total U.S. electricity consumption. Through basic research advances in organic and inorganic light-emitting materials, solid-state LEDs with efficiencies nearing 50% may be attainable for large area diffuse illumination as well as local, high brightness sources. Replacement of today's less efficient fluorescent and incandescent lighting would translate into a huge energy savings, with an associated reduction in carbon emissions from the energy points of origin. Other relevant examples where innovative materials could lower energy consumption include phase-change materials as structural building elements and smart electrochromic windows. Such "active" materials systems would respond to climatic/lighting changes to substantially reduce the energy spent on space heating and cooling (~35% of residential energy use).

New Scientific Opportunities

The undisputed need for new approaches to harness, manipulate and conserve energy in the commercial, residential and industrial sectors dictates that basic research on innovative functional materials for energy technologies be adopted as a high priority element of the BES portfolio. This is because, almost invariably, the path to commercial realization of visionary energy technologies is obstructed by materials limitations. Application of powerful, state-of-the-art synthesis, molecular level processing, and computational modeling methods to address these key materials challenges affords exciting opportunities for future basic research within DOE. Specific examples of energy technologies that might be enabled through such basic science efforts include:

- high efficiency (~50%) organic LEDs for solid-state lighting,
- high efficiency (~30%) nanocomposite solar cells for electricity generation,

- low cost catalysts & high selectivity membranes for stationary fuel cells,
- thermoelectrics for waste heat utilization, self-powered thermal sensors and spot cooling,
- high energy density, high power density solid-state rechargeable batteries,
- reinforced lightweight composites for load-bearing applications,
- high sensitivity/selectivity sensors for optimizing energy usage,
- functional materials for high temperature/highly corrosive environments,
- membranes for high efficiency chemical phase separation,
- phase change materials for thermal energy storage in building envelopes,
- flexible, transparent, thin film conductors for organic LEDs, organic photovoltaics, and electrochromic windows,
- nanocomposite hard and soft magnets for sensors, electric motors, actuators, transformers, and magnetic refrigeration, and
- biomimetic molecularly-based energy storage.

Below, more detail is provided for several of the above technological examples, emphasizing how a new generation of materials, constructed in a bottom up fashion from molecular- and colloidal-scale building blocks, allows for independent tuning of different materials properties that might normally be coupled or otherwise difficult to realize.

As one illustrative example, self-assembled nanocomposite materials incorporating semiconducting nanorods and a hole-conducting polymer offer great promise for achieving low-cost, high-efficiency solar cells, wherein the rod diameters and lengths could be adjusted to match the bandgap to the solar spectrum, while the rod location and orientation could be controlled in the organic hole-conducting polymer matrix to deliver electrons and holes to their respective electrodes. By combining rods suitably, it may be possible to make multibandgap tandem cells with efficiencies rivaling those of the high end solar cells currently used in satellites, but instead manufactured by very high volume methods, such as roll-to-roll processing. Tandem cells of nanorod arrays with varying rod diameters, for instance, could allow efficient capture of low energy photons, while transmitting the high-energy end of the solar spectrum that could then be efficiently harvested using an array of shorter nanorods. Development of new processing technologies for rapid, large-scale manufacture of such devices, as well as low cost synthetic routes to the conductive organic and inorganic nanorod components, is paramount if the goal of affordable solar cells with conversion efficiencies of 30% or more is to be achieved.

Consider, as another example, a thermoelectric material that provides independent control of the thermopower, and of the electrical and thermal conductivity (a so called “phonon glass” but electron conductor). A quantum dot superlattice of isoelectronic materials with many interfaces could perhaps provide independent control of the electrical and thermal conductivity, while controlling the degree of doping to place the Fermi level near a peak in the electronic density of states could be used to enhance the thermopower. The tenability of such a material and the development of a low cost processing technology represent large materials development challenges.

High interface per volume materials offer other special advantages in the energy storage arena as well, particularly for advanced secondary battery technologies. For instance, nanoscale active electrode composites (Li-alloying metal nanoclusters, Li-insertion metal oxide or metal phosphate nanoparticles) self-assembled in a polymer ion-conducting matrix could enable all solid, thin film batteries capable of high

current rates, while accessing the full theoretical capacity of the active electrode material. The use of nanoscale active components offers further promise to dramatically extend cycle life of rechargeable batteries by enhancing stability to volumetric excursions that cause decrepitation of bulk electrodes.

Molecularly designed organic or nanocomposite materials also hold new opportunities for building-integrated thermal storage based on solid-solid phase transitions. Here the challenge is to find inexpensive materials systems that exhibit inherently high heat storage capacity over a tunable temperature range with minimal cyclic expansion/contraction through the phase transition and no special isolation requirements. Despite the tremendous potential savings in energy such a technology could offer (space heating/cooling represents 35% of residential building energy use), materials studied to date for this application have been relatively primitive, off-the-shelf systems (e.g., paraffin). Bringing the full force of recent materials advances to bear on this technology challenge could yield a tremendous payoff in reduced energy consumption.

Finally, light weight reinforced composites could be envisaged where constituents could be added for control of special physical and mechanical properties. Such materials would have a combination of different functional properties in addition to providing load-bearing capacity.

In the development of such functional nanostructured materials, computer simulation will likely play an increasingly important role. Electronic structure calculations, for example, can be used to predict the electron and phonon energy states in nanocrystals and how they differ from their parent 3D bulk materials, thereby enabling the first-principles design of a material's optoelectronic properties. Similarly, recent years have seen great progress in describing the properties of systems of long chain molecules through computational approaches such as advanced Monte Carlo and molecular dynamics methods, self-consistent field models and phase-field calculations. Modeling the equilibrium and transient behavior of polymer/ inorganic nanocomposites of the types discussed above is made challenging by the enormous range of relevant length scales (angstroms to millimeters) and time scales (picoseconds to days) that characterize the structure and motion of the different components.

Relevance and Potential Impact

Much of the basic research in materials called for in this PRD could directly benefit existing applied energy programs under the DOE. Especially, specific efforts such as sensors, phase-change building materials and materials for solid-state lighting could feed into the DOE's Energy Efficiency program. Similarly, nanocomposite-based solar cells, materials for fuel cells and novel energy storage materials could nourish the DOE's program on Renewable Energy. For most of the innovative materials concepts discussed herein, the impact of each materials breakthrough would affect multiple energy technologies, and in some cases, extend well beyond the interests of DOE, such as for lightweight reinforced composites.

Estimated Time Scale

Experience in the materials industry has taught that commercial development of new materials is a long and often costly process, requiring typically about 10 years from the earliest development stages to full commercialization. One can project that a similar time frame might be needed to lay the basic scientific foundations underpinning the energy-related materials technologies described herein, given that sufficient, dedicated monetary resources were made available. This inherent lag time to payoff argues for immediate DOE investment, if energy security is to be effectively addressed within the next decade. It must be

emphasized that the vision here is not incremental, but encourages the possibility of discovering entirely new ways of harnessing, manipulating, converting, or conserving energy. It is critical that appropriate long-term investments be made to guarantee advances in functional materials for future energy technologies.

MULTILAYER THIN FILM MATERIALS AND DEPOSITION PROCESSES

EXECUTIVE SUMMARY

Multilayer thin films consisting of nanoscale microstructures exhibit a wide range of superior physical properties, which have found many applications in the residential, commercial and industrial sectors. One example is the use of thin film multilayer coatings on glass, with the film thickness in the range of 5- 50 nm, to reduce heating energy use in buildings. These coatings can reduce heat loss in winter (up to 30%) and heat gain in summer through windows. (Windows in buildings account for about 4% of all U.S. energy consumption, at a cost of about \$30 billion/yr.) Other applications based on multilayered structures include, but are not limited to, wear- and erosion-resistant coatings, magnetic recording media, and reflective x-ray mirrors. These applications are mainly driven by the significant improvement in properties derived from the manipulation of nanoscale structure. In order to propel new scientific revolutions in the application of multilayer thin film materials, significant advances in the design, synthesis, and deposition of these nanoscale multilayers need to be achieved. The major research directions proposed involve (1) development of a new generation of coating materials with optical, photochemical, and other functionalities; (2) creation of explicit mechanistic models that allow precise control and prediction of coating properties based on deposition conditions and film growth chemistry/kinetics; and (3) development of the next generation of thin-film deposition techniques and in-situ characterization tools.

Summary of Research Direction

The performance of many materials in buildings is influenced by surface optical and thermal properties. This is most readily apparent in surfaces that influence selective solar energy transmission, absorption and rejection. Conventional solutions for energy control are often based on manipulation of bulk materials properties. Modified surface properties can effectively control radiant energy flows. The ability to modify surface properties using specific coating structures and chemistry could provide exciting new energy control functions.

One important class of surface coatings is based on thin film multilayers. Historically multilayer coatings were applied in small areas at high cost (e.g., multilayer antireflection coatings on lenses at costs of $> \$1,000/\text{m}^2$). Over the last 20 years a variety of new controllable, high rate, deposition technologies have been developed that are capable of producing very high performance multilayer coatings at low costs, $\$0.10$ - $\$10.00/\text{m}^2$. Existing deposition processes include sol gel, evaporation, sputtering, chemical vapor deposition, etc. Coatings may range from 5-5000 nm in thickness, with stacks which may range up to 50 layers. Each deposition process has strengths and weaknesses with respect to available source materials, coating thickness and uniformity, deposition rate, film stoichiometry, morphology and microstructure, etc. Several of these production processes have been adopted on a very large scale. For example, low-emissivity coatings with 5-20 layers with a total thickness of 60-150 nm are manufactured in volume ($50 \text{ Mm}^2/\text{yr}$) by reactive magnetron sputtering on sheets of glass 3 x 4 m and on plastic webs 2 m wide.

A new generation of products based on thin film coatings is currently being researched, including:

- electrochromic window coatings that dynamically control sunlight transmission;
- photovoltaic devices to convert sunlight to electricity;

- touch screens for input to computer systems; and
- organic light emitting diodes for energy efficient lighting.

Although commercially viable processes are available for some applications, there are seemingly fundamental limitations to each process that constrain its applicability. Most of the deposition processes involve complex chemical reactions (e.g., CVD) or energetic plasmas (e.g., sputtering). Current thin film process technology is based on semi-empirical experience in optimizing these complex deposition processes rather than a first principles model of the process that would allow a “materials-by-design” approach to new coating developments. Furthermore, optical properties of materials used in these coatings are often highly dependent on deposition conditions (e.g., substrate temperature, pressure, gas flow rates for reactive sputtering).

New Scientific Opportunities

Coating Materials and Systems. A first generation of static optical coatings (coatings that reflect long wave radiation, and spectrally selective coatings that reject solar infrared radiation) are well established in the marketplace. These are based largely on silver-based sputtered coatings that are antireflected to increase transmittance using dielectric layers. There are numerous additional energy efficiency applications for buildings that will benefit from an aggressive effort to develop and synthesize new materials systems for these applications. One of the more interesting but challenging opportunities is the development of a new generation of optically active electrochromic windows in which a small control voltage can induce a large change in optical density. First generation prototypes are emerging but do not yet meet functional and cost requirements. Novel materials systems could provide enhanced performance, longer life and lower production costs. Dynamic redirection of sunlight using optically active coatings is a challenge that has not yet been achieved. Holographic coatings or layers with controllable index of refraction might provide suitable control mechanisms. Transparent conductive coatings that meet functional objectives and other energy control functions, as well as cost objectives for organic LEDs, remain technical challenges.

Deposition Systems. A key breakthrough and enhancement of thin film deposition systems would extend industry’s current large investment in these production facilities. A primary objective would be the creation of explicit mechanistic models that allow prediction of coating properties based on accurate models of deposition conditions and film growth chemistry and kinetics. Currently, process parameters are determined by empirical “tweak and look” approaches that offer little opportunity for breakthroughs in materials design. Understanding the close relation between manufacturing process parameters and the local thermophysical and chemical environment at the point of film nucleation and growth, and the resultant bulk and surface properties of materials, is crucial for a breakthrough in the progress in coating developments that could lead to the next generation of thin film technologies. Modifications to conventional deposition approaches can provide the ability to achieve new film properties using “conventional” materials. Energetic deposition by Filtered Arc or by Pulsed Magnetron sputtering with biasing techniques, for example, is an emerging technology for the formation of smooth, dense films that show improved adhesion, enhanced refractive index in the case of oxides, and diamond-like bonds in the case of carbon. Another example is the development and application of a plasma-assisted sputter source that can increase the deposition rate, thus reducing costs, and can improve the stoichiometry of compound films used in multilayers. Some deposition processes with these new capabilities might be inherently unstable and require real time process control to achieve and maintain optimal deposition conditions. A new generation of sensors that provide real time, in-situ optical, chemical and spectroscopic information may be required.

Relevance and Potential Impact

The combination of novel materials produced using these more versatile deposition systems could provide revolutionary advances in optical coatings for energy efficiency in buildings. Because they build on existing industry experience with related technologies they have the potential to be widely adopted by industry, once the basic R&D problems have been solved.

There are numerous opportunities to use high performance thin film coatings to reduce energy use in buildings. For example, heat loss and heat gain through opaque building surfaces occur in part because of the surface radiative properties which can be readily controlled using thin film coatings. Energy flows through glazed openings are even larger and can also be controlled using coatings on glazed surfaces. One example is control of cooling loads through windows. Approximately 1 quad of resource energy worth about \$10 billion/yr is directly associated with cooling performance of windows. An equivalent amount of energy could also be captured if daylighting systems displaced electric lighting in the perimeter zones of buildings.

Estimated Time Scale

Initial useful results could be achieved by an aggressive program in 3-5 years. To further improve coating performance and processes that will increase durability and manufacturability as well as enhance the required energy control properties, 5-10 years might be required.

Cross-Cutting Research and Education

Nanomaterials

**Preparing Tomorrow's Workforce for the Energy Challenge
and Heightening the Public's Awareness**

NANOMATERIALS

EXECUTIVE SUMMARY

New materials engineered on the 1-100 nanometer length scale will play a vital role in future energy technologies. It is on this length scale that the electrical, thermal, mechanical, optical, and chemical properties of materials have always been determined. As nanoscale science and technology are developed, new materials of revolutionary capabilities will emerge. High temperature superconductors and strained-layer superlattices are two current examples of nanoengineered materials of great energy relevance. Single-walled carbon nanotubes in their various forms are among the leading candidates for future examples. They have properties that could lead to transforming advances in fuel cells, batteries, capacitors, nanoelectronics, sensors, photovoltaics, thermal management, super-strong lightweight materials, hydrogen storage, and electrical power transmission. Continuous fibers composed of single-walled carbon nanotubes of a specific type (the so-called “armchair” tubes) are expected to have an electrical conductivity similar to copper, thermal conductivity similar to diamond, and a tensile strength 10-100 times higher than steel while having only 1/6th the weight. Since the carbon nanotubes behave as individual, ballistic quantum conductors along the tube axis, but have much less conductivity perpendicular to this axis, eddy current losses in the macroscopic spun carbon nanotube wire may be vanishingly small. When a practical scheme is developed to produce these nanotube “quantum wires” at a large scale and low cost, they may replace the copper windings in electric motors, and enable electric power transmission lines of much greater length and efficiency than currently possible. Support of the underlying basic science that leads to such new nanomaterials should be a prime objective of basic energy research.

Summary of Research Direction

Basic research within the DOE Office of Science has always concentrated heavily on the challenge of discovering new materials and understanding their behavior at a fundamental level. Over the years this research has concentrated increasingly on the nanometer length scale, to the point that now it is hard to find an important materials research topic that does not qualify at least broadly as nanoscale science. During the course of this workshop it became abundantly clear that nanoscale materials science continues to be of critical importance in the future of all energy technologies. In many cases it is the single most limiting issue.

Rather than summarizing the vast range of new opportunities in nanomaterials, this cross-cutting PRD will focus on just one: single-walled carbon nanotubes. The possibilities with just this one line of research are enough to occupy researchers for decades to come.

New Scientific Opportunities

Single-walled carbon nanotubes (swnt) can be visualized as sort of nanoscale soda straws formed from a single atomic layer of graphite cut into a long strip, then curled up and sealed seamlessly along its length to form a long hollow tube about one nanometer in diameter. The ends of the tube can either be open or closed with a hemispherical dome of carbon to form a closed hollow molecule that is a member of the fullerene family – it is an elongated “buckyball”. These swnt molecules can, in principal, have any length from a few nanometers to many meters in length, although typical methods now make them a few microns long. The longest ones prepared thus far by any method are no more than a few millimeters in length. Since the graphene sheet has the highest Young’s modulus of any material, these carbon nanotubes have

both a high longitudinal extensional modulus (~ 1 GPa), and an extremely high bending stiffness. When forced to bend or twist the tubes buckle, much like a soda straw. But when the stress is relaxed they are found to snap back straight with no damage. In addition to this extremely high bending toughness, the tubes are predicted to have an exceedingly high tensile strength in the range of 10-100 times higher than steel, but with a density of only 1.3 g cm^{-3} .

It is perhaps best to think of these tubes as a new polymer, a follow-on to nylon, polyethylene, or Kevlar. Like these earlier feats of polymer engineering (which are themselves marvelous examples of nanotechnology), the new single-walled carbon nanotubes can be made from cheap gas phase carbon feed stocks such as methane or carbon monoxide, using a catalyst that stays attached to the “live” end of the growing polymer. Over the past decade methods have been developed to produce these tubes with good quality in gram amounts, and thus far with slightly lesser quality in kilograms. With intense research it is reasonable to expect that large-scale industrial production of this new all-carbon polymer will be possible at low cost, and that over time revolutionary new catalysts and processes will be found to produce swnt with precise control of length, diameter, and type, similar to the revolutions that have occurred in polyolefin production in the last century.

Each swnt “buckytube” is uniquely specified by a pair of small integers (n,m) which define just how the strip of hexagonal graphite is cut. The diameter of the tube ranges from 0.6 to 3 nm depending on the sum of the two integers, $n+m$, while the electrical properties of the tube depend on the difference, $n-m$. If $n-m=0$ the nanotube is a one-dimensional metallic conductor. If $n-m = 3, 6$, or some higher multiple of 3, it is a semi-metal. Otherwise, if $|n-m| \bmod 3 > 0$ the tube is a direct bandgap semiconductor with a bandgap in the range of 0.8-1.4 eV, depending on the exact values of n and m. Just as with more traditional direct bandgap semiconductors, such as GaAs, these semiconducting nanotubes have been found to be good light emitters directly across the bandgap, except here they do this on a nanometer scale. The semiconducting tubes have been used to produce the world’s first single molecule transistor, operating in air at room temperature.

The $n=m$ metallic tubes, which are termed the “armchair” tubes because their open ends resemble the arms and seat of a chair, are now known to be sensational electrical conductors, rivaling copper. They are such good conductors because they are quantum “light pipes” for electrons, and they have extremely long coherence lengths. Current calculations indicate that an electron traveling in a ballistic quantum wave packet down one armchair tube can hop onto an adjacent armchair tube with no loss. If this turns out to be true in practice, we may find that a fiber spun from all armchair swnt tubes will have an electrical conductivity similar to copper while having only $1/6^{\text{th}}$ the weight. Such a bucktube quantum wire should have extremely small eddy current losses since the transport properties are good only as long as the longitudinal momentum of the electron is conserved. Experiments have already shown that swnt can be spun into continuous highly aligned fibers from a sulfuric acid spinning medium, much like Kevlar. It may be possible to develop such a technology on a mass scale. These armchair quantum wires may someday be the logical replacement for copper and aluminum wiring throughout commercial and domestic applications

Relevance and Potential Impact

The fact that these swnt buckytubes are the best electrical conducting polymers that we have ever discovered suggests they may be involved in revolutionary improvements in nearly every technology where electrons flow (e.g., fuel cells, batteries, capacitors, photovoltaic devices, memories, logic, and interconnects

in computers and sensors). If the armchair quantum wire has the properties projected above, and if it can be made in large amounts at low cost, it may enable a truly worldwide electrical energy grid.

Space Based Solar Power. NASA has recently taken a fresh look at the notion of solar power satellites, and this notion has been the focus of an NRC study. There is plenty of power to be had from space in geosynchronous orbit, easily the additional 10 TWe that is expected to be needed by the year 2050. However, to make this economically feasible breakthroughs must be made in a wide range of technologies. Nearly all of which could be facilitated by nanomaterials; especially those made with single-walled carbon nanotubes.

Carbon-nanotube-based materials may enable dramatic reductions in the weight of rockets and aerospace vehicles. They may enable construction of huge structures in space, including the structural support, the PV arrays, transport of waste heat to thermal radiators, and the field emitters used in the high power microwave generators. Through their use in nanoelectronic computers, memories, and sensors they may enable dramatic developments in autonomous robots that, with artificial intelligence, are able to construct and repair these huge, complex, orbiting structures. The swnt will be useful as well in construction of the necessary rectenna arrays on earth, and the electrical power transmission grid and local energy storage that handle the power beamed down from above. Also enabled will be the notion of Lunar-based solar power. This may very well be the way the world's energy challenge is finally met by the year 2100.

Estimated Time Scale

Major developments in the first commercial swnt applications may be expected within the next few years. Applications in fuel cells, supercapacitors, lithium ion batteries, flat panel field emission displays, and electromagnetic interference (EMI) shielding will likely happen within the next 10 years. Continuously spun swnt fibers and "quantum wires" may also be available within this time period. Full realization of the opportunities afforded by swnt could still be unfolding decades in the future.

PREPARING TOMORROW'S WORKFORCE FOR THE ENERGY CHALLENGE AND HEIGHTENING THE PUBLIC'S AWARENESS

EXECUTIVE SUMMARY

This proposed research direction aims at attracting a critical mass of students in physical sciences and engineering to take up the energy challenge, and at raising the awareness of the public, including scientists, in today and future challenges and opportunities in energy.

There is an urgent need to cultivate basic research in energy and to redress the balance of the number of students in physical sciences and engineering. The proposed research direction offers the opportunity to achieve world class education and technical training by communicating the joy and excitement of the energy challenge to young adults, thereby raising the pupils' awareness and inspiring them with unique and exciting missions that will meet their life idealism and career ambitions.

To achieve these goals, it is suggested that DOE compile background material on the theme "In Search of Terawatts." Background material includes, for example, PowerPoint slides highlighting the grand challenges in energy for this century, both from a scientific/technological and societal perspectives. This background material will be prepared by DOE staff and will be distributed to DOE-supported scientists. It will constitute the basis for public talks intended for primary and secondary schools, universities, and other public places.

Though it is acknowledged that the National Science Foundation already invests massively in educational programs, it is believed that the paramount magnitude of the energy problem and its urgency justifies that DOE undertakes this proposed research direction.

Summary of Research Direction, Relevance and Potential Impact

The challenge in securing clean, cheap and abundant energy for this century has long been overlooked. Responding to this challenge is both time-critical and complex.

Today, globally energy consumption is 13 TW per year, 25% of which is consumed by the American population. Experts and scholars agree that annually 50 TW of energy will have to be produced to supply enough energy to the 10-12 billions worldwide population expected in the year 2050. None of today's technologies or a combination of them can fulfill this demand. In fact, meeting the Terawatt Challenge, while complying with environmental requirements, will necessitate not only revolutionary scientific breakthroughs but also the mobilization of a critical mass of high skilled researchers, scholars, and students, as well as the continuous support from the general public. Preparing tomorrow's workforce to the energy challenge and educating the public are two enabling forces that support and complement research and development in energy.

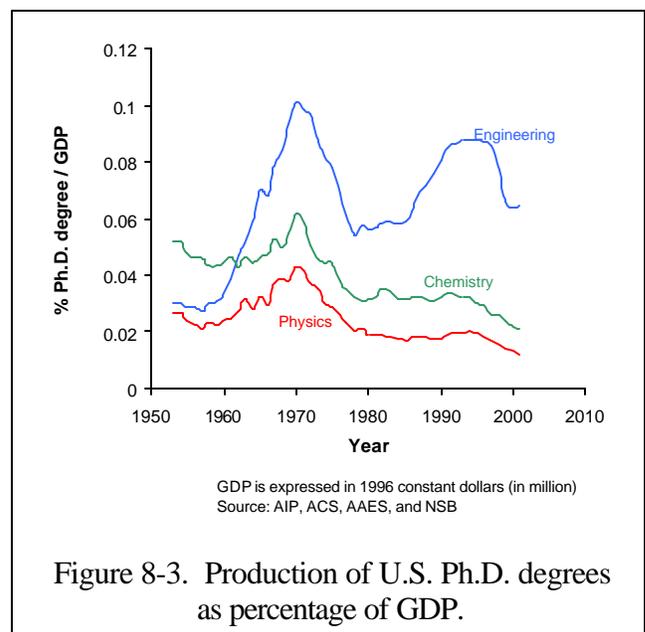
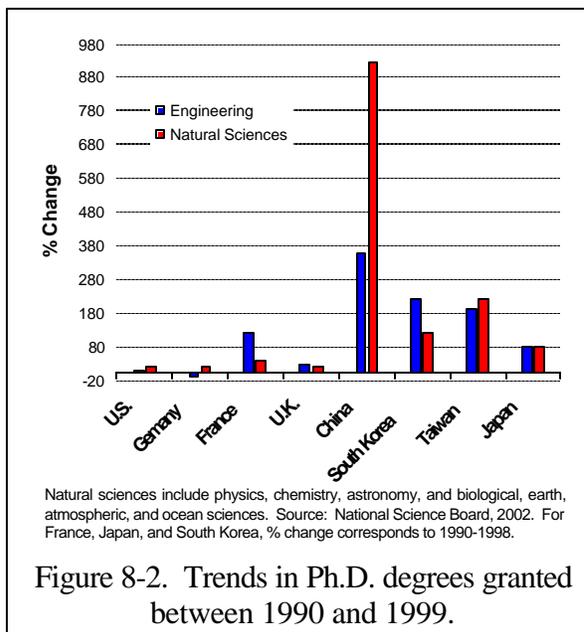
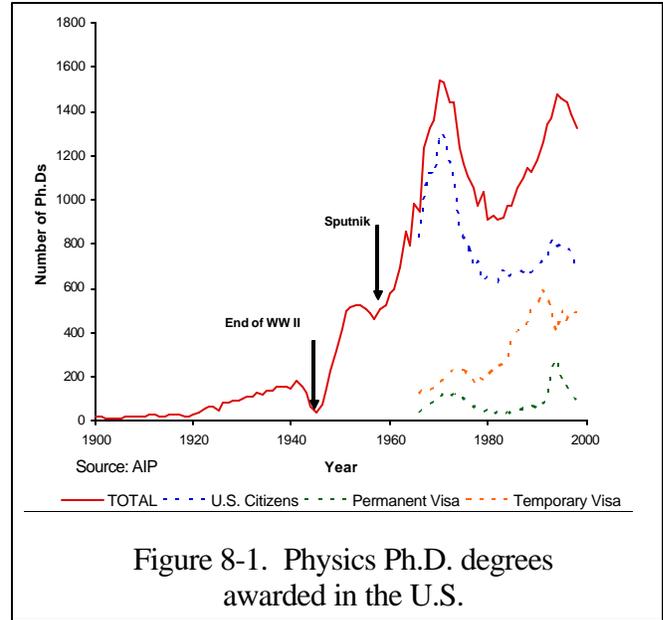
In other words, strong human capital and outstanding technical talent are some of the many potential game-changers for securing our energy future and strengthening U.S. international competitiveness and leadership. The success in achieving this goal relies heavily on our ability to attract the best students in physical sciences and engineering and to attract them in a large enough quantity.

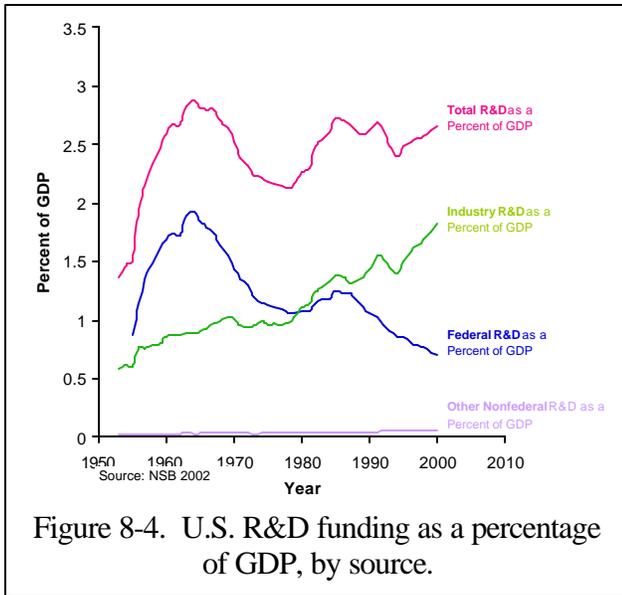
During the 20th century, massive federal investments in basic and applied research after World War II and the Sputnik mission have greatly contributed to the growth of the number of scientists and engineers, as

illustrated in Figure 8-1. In the mid-1990s though, the growth was mostly due to the influx of foreign-born students, mostly from China. Today, nearly half of the total number of U.S. Ph.D. degrees awarded every year in physics is earned by students coming from overseas.

The American higher education system is losing its edge in educating scientists and engineers. Figure 8-2 indicates that the U.S. has had one of the lowest growths of Ph.D. degrees in engineering and natural sciences between 1990 and 1999. China is greatly contributing to the worldwide growth of scientists and engineers. The same trend is observed at the undergraduate level. In fact, the number of students in engineering and natural sciences at the bachelor level increased by a factor of 1.4 in the U.S. between 1975 and 1998, while that of Pacific Rim tripled over the same period of time. For the first time, the pool of scientists and engineers worldwide is expanding faster in the Pacific Rim than in the U.S.

Clearly, the production of U.S. Ph.D. degrees in engineering, physics and chemistry (including U.S. and non-U.S. citizens), normalized to the gross of domestic product, has drastically decreased since the 1970s, reaching ever-lowest levels in 2001 (Figure 8-3). During the past decade only, the number of U.S. graduate students has decreased by 26% in physics, 19% in mathematics, and 10% in chemistry. Engineering though experienced a modest growth between 1885 and 1992, but has fallen since then.





The decline in the number of the U.S. graduate students in physical sciences and engineering is directly linked to the disinvestment of the federal government in research and development (Figure 8-4). The federal share of total U.S. R&D funding has decreased from 65% in 1965 down to 26% in the year 2000. Today, more than half of the U.S. R&D funding comes from the industrial sector, emphasizing the development of new products at the expense of basic discoveries.

The same trend applies for public investment in energy. The federal government has drastically disinvested in energy R&D during the 1980s. In the year 2000, the energy share of the total federal R&D budget was 1.4%, compared to 12% in 1980.

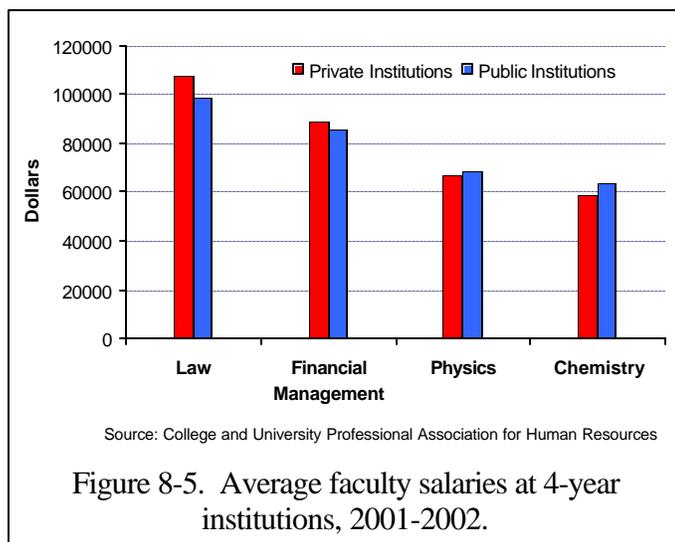
In addition to the burdensome decline in the number of American students in physical sciences and engineering, the U.S. will soon experience difficulties in renewing its highly qualified technical workforce. The energy industry has long experienced difficulties in recruiting trained workforce. Moreover, the scientist/researcher labor pool is ageing. The total number of retirements among workers holding degrees in science and engineering will increase significantly over the next 20 years. Meanwhile, the demand for physical scientists and engineers by the year 2010 will increase by 18% and 9%, respectively, according to the U.S. Bureau of Labor Statistics.

The decline of student enrollment and the relatively low attractiveness of scientific careers will make it difficult to renew the U.S. skilled workforce. For example, academic positions in physics and chemistry are financially poorly rewarded, as illustrated in Figure 8-5. The average faculty salaries in chemistry and physics departments is 20-46% lower than those in law and business schools.

In summary, federal disinvestment in science and engineering basic research, skills shortage and low attractiveness of scientific careers are weaknesses that are likely to hamper the rate of innovation, thereby undermining U.S. competitiveness over the coming decades.

There is a pressing need to reverse these trends: Strong human capital and skilled workforce are key assets to maintaining U.S. leadership in a knowledge-driven world economy.

It is recommended that DOE play a key role in raising the awareness of scientists, students, and the general public in the energy challenge



and education issues. This can be achieved by compiling some background material in forms of PowerPoint slides on the theme: "In Search of Terawatts." This background material will include data and facts on energy that will reflect the needs for today and tomorrow's scientific grand challenges, both at the academic and industrial level. It will include, for example, data on funding research in physical science, energy consumption, production cost of electricity by source (coal, nuclear, gas, oil, wind, solar, and geothermal), energy reserves, energy costs versus efficiency, energy conversion, storage and distribution, population growth, and environmental issues. This background material will be distributed to DOE-supported scientists to help them build public talks for K-12 students, undergraduate students, teachers, scientists, and the general public.

Mass communication of the energy challenge to a broad audience will likely generate informed interest among the public and, more importantly, among the student community.

This proposed research direction, "Preparing Tomorrow's Workforce for the Energy Challenge," will have unprecedented impact on the realization of the scientific endeavor for solving the single most important challenge of this century: producing annually 50 TW of clean, cheap, sustainable and abundant energy by the year 2050.

Such an initiative will captivate the imagination of children, students, teachers, researchers and the public, and therefore contribute to developing the garden of science. If appropriately funded and supported by federal agencies, this could have a similar impact as that of the Sputnik mission.

Sources

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American Institute of Physics (AIP)

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American Association of Engineering Societies (AAES)

College and University Professional Association for Human Resources

Energy Biosciences Research

Energy Biotechnology: Metabolic Engineering of Plants and Microbes for Renewable Production of Fuels and Chemicals

Genomic Tools for the Development of Designer Energy and Chemical Crops

Nanoscale Hybrid Assemblies for the Photo-Induced Generation of Fuels and Chemicals

ENERGY BIOTECHNOLOGY: METABOLIC ENGINEERING OF PLANTS AND MICROBES FOR RENEWABLE PRODUCTION OF FUELS AND CHEMICALS*

EXECUTIVE SUMMARY

Emerging knowledge in functional genomics and molecular technologies provides new opportunities for the rational genetic improvement of plants and microorganisms to produce renewable sources of fuel and chemicals.

Plants are the primary producers of fixed carbon. During the past 10,000 years, plants have been extensively modified by humans to improve the production of food, feed, and fiber. An understanding of fundamental mechanisms that govern plant growth and development will allow the design of plants that can contribute to future energy security. This will require the ability to control plant architecture and composition (lignin, cellulose, hemicellulose, starch, and oils), along with improvements in the energy-efficiency of plant production (reduced nutrients, water, and land requirements) and an expansion in the range of environments that can be used for cultivation (salt tolerance and stress resistance). Improved genetic control of plants will allow production of novel biomaterials and increased efficiencies in renewable fuel production. Further advances in the fractionation of biomass into individual components using physical, enzymatic, and chemical treatments offer major opportunities for cost savings.

Metabolic engineering of new microbial biocatalysts offers the potential to produce novel biomaterials and chemicals that will serve as renewable alternatives to materials currently produced from petrochemicals. These improved microbial biocatalysts are required to expand the range of useful conditions for industrial fermentations and reduce costs through process simplification. Substantial cost savings can also be realized by the development of biocatalysts that produce enzymes (e.g., cellulase, xylanase, etc.) for carbohydrate depolymerization as coproducts during fermentation, eliminating the need for separate enzyme production facilities. Application of biochemical and genetic principles provide mechanisms for the rational design of improved enzymes concerned with the depolymerization of plant constituents and production of useful chemicals. Recent expansion in genomic sequences from microbes and plants provides a vast toolkit of genes and enzymes that can now be recombined and used to provide clean and sustainable solutions to our current dependence on imported petroleum.

Summary of Research Direction

Fossil fuel is the residue of ancient plants and microalgae that formed vast deposits of petroleum, coal, and natural gas. The ancient photosynthetic processes that produced these reservoirs of fossil energy also shaped our climate and the composition of our atmosphere. Storage of carbon in relatively inert fossil forms reduced atmospheric carbon dioxide and other compounds associated with planetary heating, and produced our oxygen-rich atmosphere. The vast scale of contemporary photosynthetic processes offers the opportunity to replace part of our dependence on fossil residues for energy and chemical feedstocks

*This document incorporates portions of the Renewable and Solar Energy Team's Proposed Research Direction entitled "To Displace Imported Petroleum by Increasing the Cost-Competitive Production of Fuels and Chemicals from Renewable Biomass by a Hundred Fold."

with contemporary sources of renewable biomass. Biological transformations of renewable biomass materials also offer the opportunity to displace current petroleum-based chemicals and plastics using renewable and environmentally-friendly processes.

Approximately 0.2% of the current U.S. energy needs are supplied by renewable biomass, principally direct combustion (heating or electricity) or ethanol as a fuel extender and oxygenate (providing 2 billion gal/yr or 1.3% of total automotive fuel). Because of advances in genetic technologies, there are major new opportunities to increase the primary production of fuel and chemical feedstocks by genetic modification of plants for increased yield of useful constituents. In addition, there are important opportunities to improve technologies for the solubilization and conversion of plant constituents by the application of our emerging knowledge of microbial genomics. Broad implementation of biomass as a primary energy source in the U.S. and elsewhere will depend upon the genetic modification of plants to expand the range of soil environments for productive cultivation, to minimize nutrient requirements, and to increase crop productivity (tons/acre per year). These improved plants will become the feedstocks of the future. This is a long-term goal where sustained investment in fundamental research is essential. Results from these investigations will serve as a guide for the rational design of future improvements using a combination of traditional and molecular approaches.

To realize significant increases in primary biomass production, a systematic research program on plant metabolic engineering is imperative. An important objective should be to understand the mechanisms involved in the synthesis of cell wall polymers that are the principal constituents of biomass. Additionally, a focus on metabolomics, enzyme design and engineering, and metabolic modeling will be integral to achieving improved primary productivity of biomass and chemical feedstocks derived from carbohydrates or lipids. Understanding the factors that control plant adaptation to the environment and disease will also be important to maximizing yield and allowing the utilization of marginal land for biomass production. Areas of particular interest include salt tolerance, metal tolerance, and more efficient use of water and nutrients.

Research on microbial systems should focus on the development of improved bioconversion processes to produce chemicals (ethanol, longer chain alcohols, fatty esters, etc.) that can be blended with currently used automotive fuels (gasoline, diesel) and on the development of microbial processes for higher value coproducts (commodity chemicals, bio-based plastics) that displace petroleum and increase revenues. Under-utilized residues from agriculture and forestry, with little or no current value, represent a potential source of feedstocks for this area of application. Approximately 30 million tons of corn is currently converted to fuel ethanol in the U.S. by a mature industry using very efficient processes that take advantage of the highly digestible nature of starch by microbial enzymes. While this can continue to expand and make an important contribution to the energy security of our nation, the energy intensive nature of corn farming and competing uses of corn as food and feed will prevent the substantial replacement of automotive fuel by ethanol from corn alone. In contrast, the use of inexpensive lignocellulosic residues as feedstocks should have minimal impact on consumer costs for the primary products from agriculture (food, feed, and fiber). This new use represents an expanded benefit with minimal investment of additional energy. Additional fuels from lignocellulosics can be blended with gasoline to reduce petroleum imports while maintaining the benefits of corn-based ethanol production.

The high capital cost and increased risk associated with process complexity have thus far blocked the industrial implementation of many promising new technologies for production of biofuels and chemicals. Much of this process complexity can be reduced through the genetic engineering of improved microbial

biocatalysts, the genetic improvement of plants for specific applications, and by improvements in plant fractionation technologies that increase efficiency and reduce costs.

New Scientific Opportunities

Many aspects of process complexity can be improved by the application of knowledge from microbial and plant genomics. Genomic sequences provide a catalogue of genes that can be used to alter cellular structure, composition, and function. These sequences provide a starting point for our understanding of integrated processes that limit the growth of plants, efficiency of water and nutrient use, the partitioning of photosynthate among cellular constituents, tolerances to extreme environments, and bioconversion processes by microorganisms. An exciting opportunity is to build on this knowledge base by discovering the corresponding gene functions and physiological activities. Our increasing knowledge of plants should also support the genetic modification of plant composition for specific bioconversion processes. Understanding the fundamental mechanisms that regulate the partitioning of photosynthate between carbohydrate polymers (cellulose, hemicellulose, starch), protein, lipid, and lignin should now allow rapid improvements in modifying plant composition for fuels and chemicals. For instance, increasing the lignin content with reduction in carbohydrate content would increase the energy density of plant residues intended for use in combustion.

Cellulose depolymerization by enzymes is arguably the single most expensive step associated with the bioconversion of lignocellulose to fuels and chemicals. Increased understanding of the molecular mechanism of glycohydrolases may lead to creation of more efficient enzymes that resist product inhibition. Additional approaches include the co-production of glycohydrolases by the microbial biocatalysts during fermentation and the co-production of glycohydrolases in the tissues of plants prior to harvesting for bioconversion. Significant reductions in added cellulase will also be achieved by improved understanding of the fundamental chemical and physical processes involved in the fractionation and solubilization of biomass.

Relevance and Potential Impact

The efficiency with which we have converted fossil biological energy sources into fuels and chemicals has allowed a tremendous expansion in population and improvement in the quality of life throughout the industrialized world. As we look toward a future that must rely upon alternative energy sources, the same fundamental biological processes that created fossil deposits and our oxygen-rich atmosphere can be harnessed to provide a renewable source of energy and chemicals. Traditional plant breeding coupled with chemical and microbial conversion processes has allowed tremendous increases in the production of food and food products over the past century. The application of the emerging field of metabolic engineering together with new advances in other areas of science and technology offer the opportunity for even greater improvements in bio-based products over the next 50 years. We envision that the application of knowledge-based methods to improvement of energy crops will provide similar gains in productivity to those realized in improvement of food crops by breeding. Increased productivity will improve the economic feasibility of growing and processing energy crops and will lead to expanded acreage of plants for energy production. We believe that a reasonable goal is to obtain a hundred-fold increase in contribution of renewable biomass (20% of energy needs) to our national security.

Estimated Time Scale

50 years

GENOMIC TOOLS FOR THE DEVELOPMENT OF DESIGNER ENERGY AND CHEMICAL CROPS

EXECUTIVE SUMMARY

Yields of usable energy per hectare of cultivated land must increase 3- to 5-fold if energy crops are to play a significant role in securing our energy future. There are no fundamental barriers to achieving the necessary gains, given a focused effort to genetically improve energy crops -- crops that will have efficient conversion of the CO₂, which is initially fixed by photosynthesis, into the specific chemical energy stores that are necessary for a particular utilization process.

Examples of the envisioned improvements in yields are as follows: from today's 3-5 dry tons/acre/yr to 12-15 dry tons/acre/yr in the upper Midwest, and from 4-5 dry tons/acre/yr to 15-20 dry tons/acre/yr in the Southeast. While yield of biomass dry matter is the single most important factor in a breakthrough to large and inexpensive supplies of biomass energy from energy crop production, other factors will also have key parts to play. These factors involve crop properties such as energy density, yield of liquid fuels (e.g., oils), and compatibility with other steps in the processes that lead from the crop as grown in the field to the final product. Reduction of the environmental impact of the entire energy cropping/energy production process is also an important goal that can be achieved through selective improvement of the feedstock plants.

Achieving these important goals will require research to dramatically improve the throughput, availability and cost-effectiveness of the genomic and informatics tools that are used to identify, functionally analyze and manipulate genetic combinations of the many genes that control critical plant properties. Recent advances in single molecule studies on DNA, including single molecule genomic mapping and single molecule sequencing, suggest that the necessary tools are within reach. These advances will both require and enable powerful new genome-centered informatics tools that have the potential to revolutionize the speed and precision of energy crop (and other plant) improvement.

Summary of Research Direction

Research in this area should: (1) develop molecular biological and other biotechnical means and databases to support efforts to aggressively increase energy crop yields; (2) emphasize especially the development of information and techniques that will speed and improve breeding and selection for high energy yields in crops (i.e., annual energy produced in the crop per unit of land area); (3) develop highly capable genomic tools for assisting the rapid development and improvement of novel energy/chemical crops and for the identification/characterization of key gene functions; and (4) map genes to guide breeding of plants with high yields and with other desired properties such as high oil content or ease of conversion to liquid fuels or high-value chemicals (e.g., chemical structures well suited for liquid fuels for the transportation sector).

This effort has four main components:

- Conduct a broad search for plants with both general and regional promise for development into energy crops;
- Develop highly capable genomic tools to accelerate the rapid improvement of these crops through conventional breeding;

- Develop tools for directed genetic engineering of critical crop properties; and
- Integrate goals for the genetic improvement of energy crops directly into the process engineering of the utilization/conversion systems that they feed.

New Scientific Opportunities

A partial listing of opportunities for scientific contributions is shown below. Elaboration of a select number of these opportunities follows in the remainder of this section.

- Genome mapping of candidate energy crops: poplar, eucalyptus, sugar-cane-like grasses, switchgrass, arundo donax (giant reed), other grasses, etc. (about 10 to 20 species)
- Bio-physical chemistry: correlating the physical and chemical processes/structures in plants to yields and to energy content or energy density, and to readiness to convert to liquid fuels or hydrogen, etc.
- Computational biology to go from basic structure to physical/chemical/biological properties to the complex factors that determine yield and energy content
- Microcalorimetry or other measurement techniques for early and fast correlation of genes to desired properties
- Extensions and correlations to and among trees, grasses, algae, bacteria, etc. on both macro and micro scales of living organisms (flora and fauna)
- Artificial chromosomes
- Genome-scale marker-assisted breeding
- Optical mapping of whole genomes
- Direct sequencing of single DNA molecules

While certain plants, such as poplar and switchgrass, have been identified as likely candidate biomass energy crops, it is not obvious which of these or other essentially wild species have the greatest potential for net solar energy conversion efficiency in a particular utilization scheme once subjected to intensive genetic improvement. This is especially true given wide variations in environmental conditions from location to location where energy crops will be needed. It is important that a number of candidate species be explored and developed in parallel and that they be differentially tailored for a set of different utilization schemes. Development programs must be conducted over the range of different environmental zones where energy crops will be needed.

The current productivity of established crop improvement programs depends upon a range of molecular tools for “marker-assisted breeding” and upon computer analyses that reveal the identity of genes that make even subtle but important contributions to plant qualities. The application of similar genomic and computational tools to the development and improvement of novel energy crops will be essential in order to obtain improvements at a pace that matches the need for developing renewable energy resources.

However, the analytic capacity of current genomic analysis tools is inadequate to support the development of multiple new species with multiple improvement program goals at multiple sites. To support the goals of energy crop improvement, these tools must become much less expensive (100-1000 fold less expensive for complete genome sequencing), have higher throughput (complete genome characterization in hours instead of years), and be more accessible (distributed in local labs instead of concentrated in centers). Genomic analysis in breeding programs must provide sufficient detail to identify the specific genes that contribute to critical plant characteristics and to manipulate their recombination at the resolution of individual genes. Recent developments such as methods for optical mapping of whole genomes and for direct sequencing of single DNA molecules offer the promise that a focused research effort can develop the necessary tools over the next half decade.

The worldwide genomics effort directed toward understanding the roles of specific genes in regulating vital characteristics of model and crop plants is continuing to identify genes that could contribute in important ways to the improvement of novel energy crop varieties. In some cases, it will be appropriate to move genes from one species to another in order to achieve specific goals. Tools for transferring genes, including groups of genes, into energy crops will be needed. For the purposes of assuring predictable outcomes and of easing the combination of transgenic with traditional breeding methods, the development of artificial chromosome vectors for energy crop species is important.

The net efficiency of energy cropping systems depends not only on the internal conversion efficiencies of the plant but also on the efficiency with which its constituents are used by the downstream processes that it feeds. In many cases it may be possible to solve difficult engineering problems in the utilization process by instead engineering genetically-controlled properties of the feedstock plants themselves. Genetic modification of feedstocks also has the capacity for minimizing the environmental impacts of the overall process. An understanding of how plant properties contribute to net energy efficiency and to environmental impacts requires a new level of integration of genetic and process engineering.

Relevance and Potential Impact

Yields of up to 3 to 5 times those now achieved in mid-scale plantings of energy crops – plantings of about 20 to 2000 acres – are needed to make energy crop fuels or feedstocks production and cost competitive with those of conventional fuels. Energy crop fuels at these higher yields would enable biomass energy to rise to a potential of 10-20% of U.S. energy, instead of the 2% role that could well be the upper bound if residues and wastes are the only feasible fuels/feedstocks. Examples of the envisioned improvements in yields are as follows: from today's 3-5 dry tons/acre/yr to 12-15 dry tons/acre/yr in the upper Midwest (Missouri, Iowa, Illinois, Wisconsin, Minnesota, and the Dakotas), and from 4-5 dry tons/acre/yr to 15-20 dry tons/acre/yr in the Southeast.

Yields of usable energy per hectare of cultivated land that is captured from solar radiation and conserved by plant photosynthesis must increase 3- to 5-fold if energy crops are to play a significant role in securing our energy future. An important element of the challenge involved in achieving these improvements is that transportation factors limit the scope of energy cropping to relatively local utilization. Another important element is that the measure of “usable energy” will depend upon whether the crop is used directly for local heat or electricity generation or is converted first to liquid fuels, methane or hydrogen. It will also depend upon details of the specific process that is involved in the utilization scheme. Different plants have different value in different processes. There are no fundamental barriers to achieving the necessary gains, given a

focused effort to develop improved “designer” energy crops with efficient conversion of the CO₂ that is initially fixed by photosynthesis into the specific chemical energy stores that are necessary for a particular utilization process.

However, all biomass energy processes incur a fuel cost – usually called fuel cost for a power plant, but feedstock cost for an industrial plant that is making a fuel, chemical or fertilizer product. The fuel or feedstock is a raw biomass material that, in the case considered here, is harvested from an energy crop. The gain of 3 to 5 required is what can bring the feedstock cost down to the low levels that can be economic for the power plant or processing plant. Therefore, the achievement of much higher yields of energy harvested per unit of farmland area is what can do the most to change the economics.

High yields are also the key to making biomass a 10-20% energy source, rather than one that is constrained by economics and by available land to a 1-5% energy role.

The number of processing steps and the difficulty of feedstock handling are also factors in the economics, and often as important or more important than the feedstock cost. Therefore the improved energy density and the improved ease of processing to final product are also important. These fuel or feedstock properties are also capable of improvement by genomic tools. The precedent of food crops today that are unrecognizable versus their wild type origins show the promise of genomic improvement via information, even without any manipulation, i.e., without genetic engineering and creation of genetically modified organisms. This research direction is the path to such productivity of desired products. It continues the normal “domestication” process and applies it to new crops and new products. The fact that the technical tools are so much improved today makes the prospect for great enhancement and true breakthroughs all the much greater.

This section includes relevance to applied energy programs (e.g., Fossil, Nuclear, Energy Efficiency, Renewable Energy, Fusion). In this case these applications are to all of the biomass energy technologies and uses within DOE’s Office of the Biomass Program. Applied to improved environmental performance and environmental remediation efforts, many of DOE’s environmental missions may also benefit from application of this research direction.

Estimated Time Scale

5-10 years: Development of genomic analysis tools with sufficient capacity to support aggressive energy crop improvement.

10-20 years: Exploitation of these genomic analysis tools in the production of 3-5 fold increases of energy crop process yields.

NANOSCALE HYBRID ASSEMBLIES FOR THE PHOTO-INDUCED GENERATION OF FUELS AND CHEMICALS

EXECUTIVE SUMMARY

Efficient synthesis of fuels like hydrogen and carbon-based chemicals from renewable sources (e.g., water and CO₂) using sunlight as the energy source, is a major opportunity for securing our energy future. The main obstacle to realizing this opportunity in direct solar conversion systems is the lack of photoactive materials that accomplish the combined task of light harvesting, charge separation, and chemical transformation with the required efficiency. Approaches based on inorganic or organic materials have many promising features, but some of the components lack the efficiency and specificity of natural systems. New discoveries over the past ten years of nanoporous inorganic, organic, and inorganic/organic hybrid structures with pore or cavity sizes in the 10-300 Angstrom range show promise for overcoming these limitations. These materials allow robust covalent anchoring of metals, organic, and biological moieties inside the pores. The potential for unprecedented efficiency lies in the tight control of the chemical reactivity through design of the reactant binding site, the controlled spatial arrangement of the active components, the traffic control of chemical intermediates imposed by the pore environment, and efficient ways to separate primary products. Substantial advances have also been made in recent years in the understanding of design principles and mechanisms of natural systems that accomplish demanding energy-related transformations, notably bacterial and plant photosynthesis. The confluence of the emerging nanoscale hybrid materials and advances in the understanding of nature's design rules of its photosynthetic and catalytic systems opens up opportunities for combining biological and inorganic/organic components in engineered assemblies for the direct photo-induced conversion of renewable substrates to fuels and chemicals at unprecedented efficiencies. A major research task involves the elucidation and understanding of the dynamics of biological components in the natural environment, which will provide a guide for the design of hybrid materials that retain the full activity of the natural component. Biological principles of chemical recognition provide insights into technologies for the nanoscale self-assembly of these hybrid structures. Another important challenge is the development of strategies for organizing the nanoscale assemblies relative to one another in order to achieve concerted, macro-scale effects.

Summary of Research Direction

The discovery over the past 10 years of novel nanoporous inorganic, organic, and inorganic/organic hybrid structures with pore or cavity sizes in the 10-300 Angstrom range and a variety of topologies has opened up new materials for efficiently accomplishing demanding chemical transformations. Key ingredients are transition metal centers or organic moieties attached to pore walls that act as active sites with specific reactivity. Controlled spatial arrangement of these sites, coupled with the molecular traffic control imposed by the pore environment on chemical intermediates, allows steering of reactions to desired products. In principle, functionalization of these porous structures can be expanded to include active biological entities, thus offering opportunities for hybrid reactors that feature the highly efficient and product-specific components of natural systems. Substantial advances have also been made in recent years in the understanding of design principles and mechanisms of natural systems that accomplish demanding energy-related transformations, notably bacterial and plant photosynthesis. Specifically, the use of novel spectroscopic, diffractometric, advanced computational, and molecular genetics tools has led to detailed insights into

structural and dynamic aspects of light harvesting, energy and electron transfer, and chemical transformations at the catalytic sites of photosynthetic systems.

New Scientific Opportunities

The confluence of the emerging nanoscale hybrid materials and advances in the understanding of nature's design rules of its photosynthetic and catalytic systems opens up opportunities for combining biological and inorganic/organic components in engineered assemblies with unprecedented efficiencies for the conversion of solar photons to fuels and chemicals. Hybrid assemblies for the efficient photo-induced conversion of renewable substrates to fuels, like water splitting to H_2 and O_2 , and the conversion of CO_2 and H_2O to methanol or other C-based fuels are a top priority. Such materials are equally expected to lead to efficiency breakthroughs in a broad range of photon harvesting, storage and conversion chemistries. This holds especially for efficient catalytic multi-electron transfer assemblies, the current lack of which constitutes a major obstacle to progress in photon energy conversion and storage, and fuel-reforming systems in direct photon conversion, photo-electrochemical, or fuel cell systems. Assemblies could range from predominantly inorganic/organic structures featuring metallic or organic active sites and just one or two biological functionalities, to essentially biological structures with only a few engineered components. Examples of current possibilities for the former include dendritic light harvesting assemblies coupled to biological or engineered transition metal centers, or mesoporous inorganic (e.g., silicate) frameworks that afford controlled spatial arrangement of covalently-anchored light-absorbing chromophores and engineered or biological transition metal redox sites. With the anticipated vigorous development of new types of nanoscale materials, new opportunities will emerge for improved coupling of light harvesting moieties with catalytic sites, channeling of sequences of reactions, and efficient ways of separating primary products. Near term examples of the predominantly biological assemblies are the generation of hydrogen by genetically engineered green algae and the use of photosynthetic reaction centers modified to produce alternative chemicals. In both cases, the separation of desired products from undesirable co-products poses challenges in the purely biological system that may be overcome by the incorporation of non-biological elements. In the case of photosynthetic hydrogen production, H_2 and O_2 are intermixed in the gas released by the algae. Hybrid systems that incorporate the unique compartmentalization properties of nanoporous supports may provide methods for separating the two gases that do not also catalyze their recombination into water.

Exploration of such hybrid assemblies will be guided by design concepts derived from natural systems, and a vigorous effort for further development of spectroscopic, diffractometric, computational, and molecular genetics tools is required for a mechanistic and dynamical understanding of the chemical transformations of natural and emerging hybrid systems. In particular, structural aspects of the matrix environment of the biological component in hybrid materials are expected to critically affect its function by influencing product release or the dynamics of substrate binding to the catalytic site. Furthermore, the conformational response of surrounding protein or membrane molecules may be critical for the activity of the natural system and, hence, an important factor to consider when incorporating biological components into artificial assemblies. Elucidation of the dynamics is still at an early stage in natural systems, and a major sustained effort is required to improve the understanding of these factors. This knowledge will be crucial for the design of hybrid assemblies.

The function of complex systems of nanoscale catalysts depends very strongly on their organization. The extremely specific molecular recognition properties of biological macromolecules suggest that they may

provide solutions to the problem of assembling these complexes. As one example, a designed sequence DNA molecule could provide the scaffold for the self-assembly of catalytic domains (biological, organic or inorganic) that are attached to sequence-specific DNA binding proteins, such as transcription factors or synthetic analogs. An important challenge is the development of strategies for organizing these nanoscale assemblies relative to one another in order to achieve concerted, macro-scale effects. For instance, a nanoscale assembly capable of catalyzing direct water photolysis may be inserted into a membrane such that H_2 is produced on one side and O_2 on the other. All of the assemblies must be inserted into the membrane in the same direction in order to achieve a large-scale production of pure H_2 .

Relevance and Potential Impact

The direct use of sunlight for the synthesis of fuels or the storage of solar energy in the form of other high-energy chemicals has the potential of playing a major role in replacing fossil fuels as an energy source. In light of the extreme variety of hybrid materials expected from this research effort, fueled by the anticipated continued rapid pace of discovery of new nanoscale structures and advances in the understanding of natural systems, the likelihood of artificial photosynthetic materials that are efficient, durable, and economically feasible is high.

Estimated Time Scale

10-20 years